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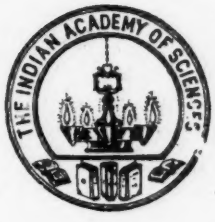

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ON THE CHROMATIC DIFFUSION HALO AND OTHER OPTICAL EFFECTS EXHIBITED BY PEARLS

By Sir C. V. Raman and D. Krishnamurti

(*Memoir No. 52, from the Raman Research Institute, Bangalore*)

1. Introduction

The present paper concerns itself with the optical phenomena observed when a pearl is illuminated by a light-source of small angular dimensions and is viewed in the reverse direction. They were briefly reported upon these *Proceedings*[1] but will be described and discussed rather more fully in the present communication. It appears worthwhile doing this, for, as was explained in the earlier paper, it is these phenomena that make the pearl appear so attractive an object when illuminated by extended light-sources.

As is well-known, the material of the pearl consists of an immense number of tiny crystals of aragonite held in an encompassing network of conchyolin. In the previous paper, the details of this structure and its optical behaviour have been discussed in detail and it is therefore not necessary to traverse the same ground here. The photographs reproduced as Figs. 21 and 22 in Plate XXVI are however of interest, as they illustrate the conclusions there stated. Figure 21 is an enlarged view of the shell of a cultured pearl as observed between crossed polaroids in parallel light. It was prepared by grinding down a fragment of the shell into a flat thin plate and mounting it in canada balsam between glass cover slips. From the birefringence pattern seen in the photograph, it is evident that the material consists of successive layers of approximately spherical shape superimposed on each other. However, the extinctions are far from being uniform, nor are the rings regularly spaced, thereby indicating that neither the optic orientation of the crystallites nor the spacing of the successive layers is completely regular. Figure 22 exhibits a small region of the same preparation as seen under a microscope between crossed nicols in parallel light; the approximately linear arrangement of the crystallites is well shown.

2. Some General Observations

It is obvious that a material consisting of discrete crystallites would be optically turbid and would strongly diffuse the light traversing it. The explanation usually given of the lustre of pearls as due to internal reflection

and/or diffraction at the surface ignores this feature and is totally inadequate. Actually, we observe three distinct effects: (*a*) the reflection and diffraction of light by the stratifications; (*b*) a chromatic diffusion halo which surrounds the direction of reflection; and (*c*) a diffusion of light through large angles consequent on a " whispering gallery effect". It is the co-operation of these three phenomena that results in the characteristic lustrous appearance of the pearl.

Figures 1, 2, 3 and 4 in Plate XXII illustrate all the three phenomena referred to above. They are photographs of a natural pearl illuminated by a light-source of small angular dimensions and viewed in the reverse direction. The pearl was not perfectly spherical and in consequence, the four figures which were recorded in slightly different settings of the pearl show recognisable differences. In Fig. 1, we observe a single spot at the centre and this is surrounded by a diffuse halo. In Figs. 2, 3 and 4 we observe two, three and four bright spots respectively, as also a diffuse halo which has its maximum intensity in the vicinity of the last of the spots. Outside the halo, there is a general luminosity which has its maximum intensity at or near the spherical periphery, thereby making the latter appear very clearly visible.

Before we proceed to describe and discuss these effects in detail, it should be remarked that they have their analogues in the phenomena observed and described by one of us many years ago[2, 3] in the case of the iridescent molluscan shells. But there are differences consequent on the fact that we are now concerned with strongly curved layers instead of plane or nearly plane stratifications.

3. THE REFLECTION-DIFFRACTION SPECTRA

The optical effects arising at the surface of a stratified medium depend on the angle at which its layers meet the external surface, as also upon the actual configuration of that surface. In the particular case when the stratifications are perfectly parallel to the external face, the incident light-waves would be reflected at that face and also at each of the boundaries between the successive strata. Since these surfaces are curved in the present case, such reflections would result in a well-defined image of the source being visible when the pearl is viewed through a suitably held lens. The image would exhibit colour consequent on the mutual interference of the reflections from the successive boundaries.

If the stratifications of the material meet its surface at an angle, the external boundary would present the aspect of a diffraction-grating, and if it

is sensibly corrugated, would give rise to a series of diffraction spectra with more orders on one side than on the other. As was shown in the case of iridescent shells and illustrated by a series of photographs in a recent paper by the present authors,[4] the sequence of spectra thus resulting would include the light internally reflected by the layers of the material as one of them, usually the last of the series. Further, the order of that spectrum would be the order of the interference of the reflections from the successive strata. In the present case, we are concerned with a convex diffraction grating and the spectra to which it gives rise would be focussed by a lens to a series of spots or streaks.

The foregoing consequences of the theory are in agreement with what is actually observed and are illustrated by Figs. 1, 2, 3 and 4 in Plate XXII already referred to. In the case of cultured pearls of good quality, the stratifications are usually so nearly parallel to each other and to the external surface that the separation of the different orders in the reflection-diffraction spectrum is very small. Careful focussing is then necessary to enable them to be seen clearly separated.

4. Nature and Origin of the Chromatic Halo

We may here appropriately refer to the phenomenon[3] of the body colour exhibited by nacreous iridescent shells when illuminated and observed in directions other than of the internally reflected light. This body colour is most vivid in directions not too remote from that of the internal reflection and then exhibits a complementary tint. It fades away in intensity and also changes colour as the direction of observation is further removed from that of regular reflection. The angle of incidence of the light on the surface of the material influences the colour of the internal reflection as also the body colour, but their complementarity when viewed in adjacent directions persists.

The chromatic diffusion halo exhibited by pearls is a phenomenon of the same general nature as the body-colour of nacreous shells referred to above, but the shape of the pearl and the curvature of its reflecting layers have important consequences. When the pearl is illuminated by a light-source of small angular dimensions and is viewed in the opposite direction, the angle of incidence of the light on the surface alters progressively from the centre outwards, and the light rays reaching the observer also make increasingly larger angles with the normal to the surface. Hence, what is observed would be an ensemble of effects; at the centre, the internal reflection would appear as a bright spot, and surrounding it would appear the

body colour with its intensity and tint changing progressively from the centre outwards consequent on the changing angles of incidence and observation.

The foregoing analogy between the chromatic diffusion halo of pearls and the body colour exhibited by iridescent nacre enables us to predict various features of the former phenomenon. The diffusion halo should in the immediate vicinity of the reflected light exhibit the complementary colour. Then again, the larger the pearl the greater would be the apparent size of the halo as observed on its surface. If the pearl is not spherical in shape, but has a different curvature in different planes, we should expect the halo to spread further out from the centre in the plane of least curvature. Complications may also be expected if the stratifications of the material are not parallel to its external surface. For, instead of a simple reflection we would then have streams of diffracted radiations emerging in different directions and these would be superposed on the diffusion halo, thereby modifying the effects observed. Hence, the chromatic diffusion halo is best studied with pearls in which the separation between the various orders of the reflection-diffraction spectrum is either zero or very small.

The origin of the chromatic diffusion halo is evidently to be sought for in the fact that the reflecting layers in the pearl are not optically continuous but consist of individual crystallites of aragonite held together in a network of conchyolin. Each crystallite would therefore function as a diffracting particle, and the light returned by an individual layer would not be confined to the direction of geometric reflection, but would be spread out over a cone whose angular dimensions would be determined by the size and shape of the individual crystallites. The distribution of intensity of the diffracted rays within such cone would necessarily also be modified by the interference of the rays diffracted by adjacent crystallites. The manner in which the crystallites are disposed in the individual layers would therefore also have to be considered. The grouping of the crystallites in parallel linear rows which appears to be a common feature in cultured pearls (see Fig. 22, Plate XXVI) is a factor which needs to be taken into account in this connection. We may, in fact, expect to find that the arrangement of the crystallites in parallel and roughly equidistant rows would give rise to specific features in the chromatic diffusion halo, as it actually does in the diffusion haloes observed in transmitted light.[1] Finally, we have also to consider that the light emerging from the material is not a simple summation of the light diffused by successive layers. The progressive changes in phase and intensity of the incident light as it advances into the material and the mutual interferences of the radiations diffused backwards by the successive layers would have to be taken into consideration. Indeed, it is only on some such lines

that we could hope to explain the complementarity of colour in adjacent directions of the reflected and diffused radiations.

5. Some Illustrative Examples

Reproductions in natural colour would be necessary to exhibit the beauty of the chromatic haloes of pearls in a satisfactory manner. However, by using panchromatic films and when necessary also colour filters, it has been possible to obtain pictures which show a fair degree of photographic contrast and exhibit the characteristic features of the halo. Twelve such photographs showing typical examples are reproduced as Figs. 9 to 20 in Plates XXIV and XXV. Individual figures amongst them illustrate the various features referred to above. For example, the influence of the shape of the pearl on the configuration of the halo is shown clearly by the circular haloes reproduced in Figs. 9, 10 and 13 which were obtained with spherical pearls. On the other hand, Fig. 11 which exhibits an elliptic halo was recorded with a spheroidal pearl, its major elongation being in the same direction as the elongation of the halo itself. Figure 14 which was recorded with a barrel-shaped specimen exhibits a certain amount of parallelism with the shape of the pearl. A characteristic feature which frequently appears is a bar of diffuse radiation along a diameter of the halo having the same colour as the iridescence, while the curved arcs on either side exhibit the complementary colour. A distinct concentration of intensity is also generally seen in such cases at the two ends of the bar. Figures 11, 15 and 16 exhibit these features and it seems highly probable that they are a consequence of the arrangement of the crystallites of aragonite in linear rows perpendicular to the direction of the bar observed.

A certain measure of optical perfection in the stratifications of the pearl and of its surface is necessary in order that the halo be regular and exhibit vivid chromatic effects. Irregularities show up quite prominently in the character of the diffusion halo. A typical example is Fig. 19 which shows a patchy appearance. Cases are also not lacking in which the halo exhibits comparatively little colour. In such cases the reflection also exhibits little iridescence, suggesting that these features are interrelated.

The diffusion of light which manifests itself in the chromatic halo clearly plays an important role in the general appearance of a pearl. It extends over a substantial area of the pearl and hence when the illuminating source is also of extended area, the reflected and diffused streams of radiation overlap. Thus, an observer would no longer perceive sharply defined images of the external luminous objects but would instead regard the pearl itself as a lustrous object. The complementarity of the colours of the reflected

and diffused radiation would compensate each other and result in a silvery white lustre.

6. THE WHISPERING GALLERY EFFECT

Figures 5, 6, 7 and 8 in Plate XXIII recorded with a natural pearl exhibit a noteworthy phenomenon characteristic of pearls. They illustrate the fact that light incident on the surface of the pearl in any direction diffuses around within the material in the plane of the stratifications with very little loss.

Figure 5 illustrates a case in which a narrow pencil of light was incident normally on the pearl and the latter was viewed from the remote side in the opposite direction. It will be seen that the pearl nevertheless appears luminous, the periphery being much brighter than the centre. Hence the effect observed does not arise from a penetration of the light *through* the body of the pearl.

In Fig. 6, the light was incident almost normally on the surface of the pearl in a direction transverse to that in which it was observed. The actual area of illumination was small and was located just behind the bright edge seen in the figure. It is evident from the photograph that the light has travelled along the periphery of the pearl in all directions transverse to the direction of incidence of the light. The slow fall in intensity of the apparent luminosity of the pearl as we move away from the illuminated spot is a noteworthy feature.

In Fig. 7, the illuminating pencil grazed the surface of the pearl horizontally at a point a little to the rear of the top of the picture. A remarkable feature of this photograph is that it exhibits no very marked asymmetry of illumination to the right and to the left. The fall of intensity of the luminosity from the top to the bottom of the picture is quite slow.

Figure 8 was photographed in the same circumstances as Fig. 5 except that the illuminating pencil grazed the surface of the pearl instead of falling on it normally. Here again, it is significant that there is little difference in intensity between the right and left halves of the picture.

The spherical shape of the pearl plays a not unimportant role in these phenomena, but it is not the essence of the matter. Long ago, it was shown by one of us[3] that when light falls on a plane nacreous shell, it diffuses far more freely in directions parallel to the stratifications than normal to them. We need not here enter into an explanation of this fact, but will content ourselves with pointing out that essentially the same property of the nacreous substance operates in the case of pearls, enabling light falling in any direction

FIG. 1

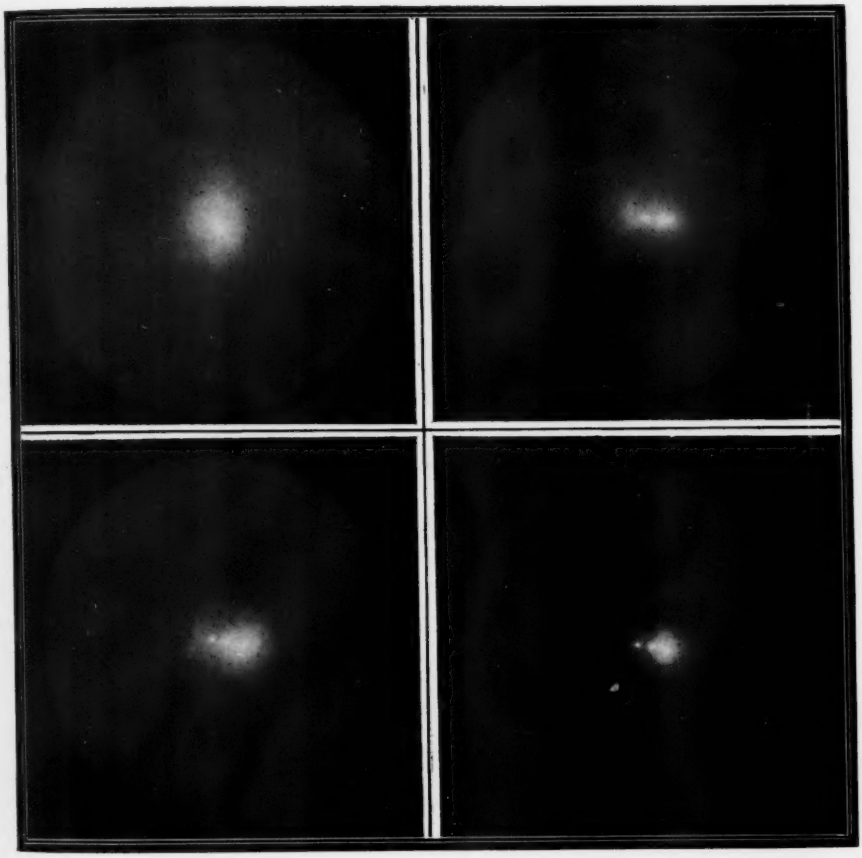


FIG. 2

FIG. 3

FIG. 4

The reflection-diffraction spectra of a natural pearl.

FIG. 5

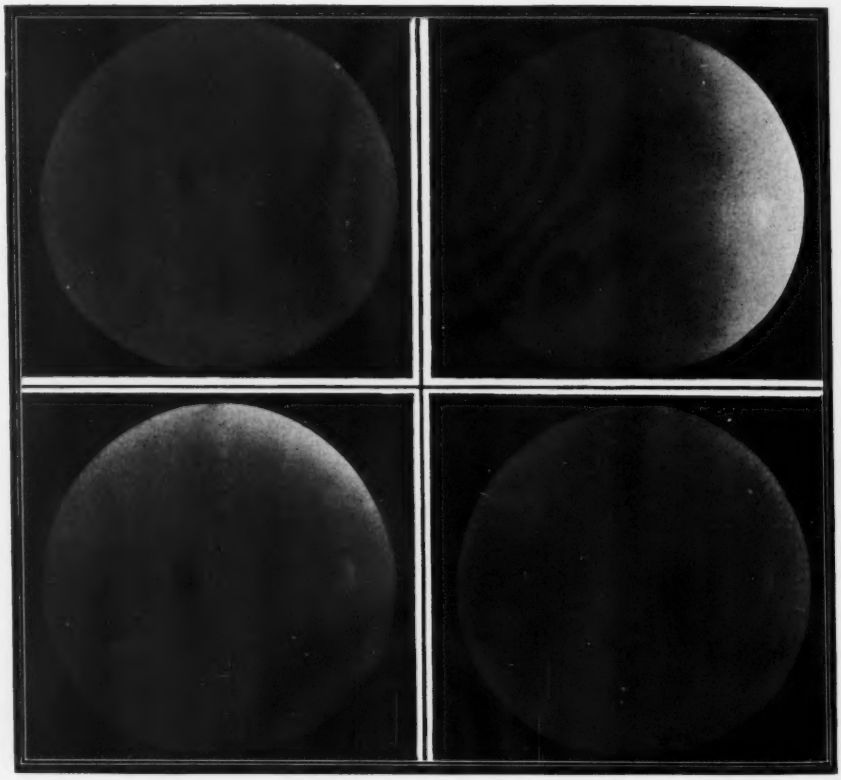


FIG. 6

FIG. 7

FIG. 8

The lateral diffusion of light in a natural pearl.

FIG. 9

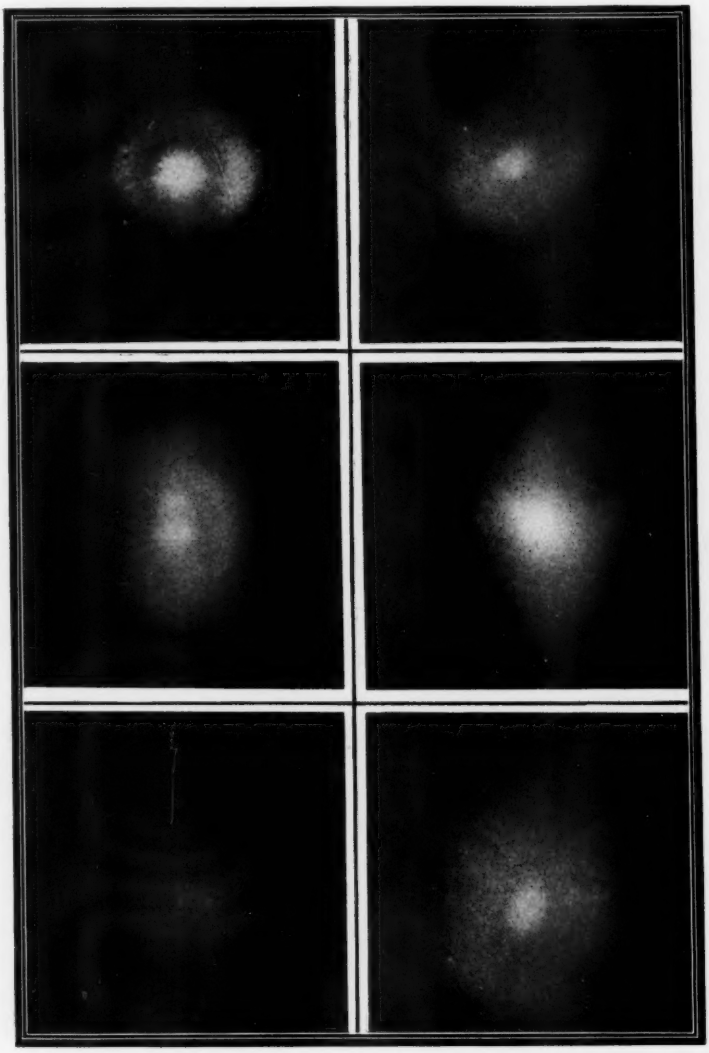
FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG 14



The chromatic diffusion halo in cultured pearls.

FIG. 15

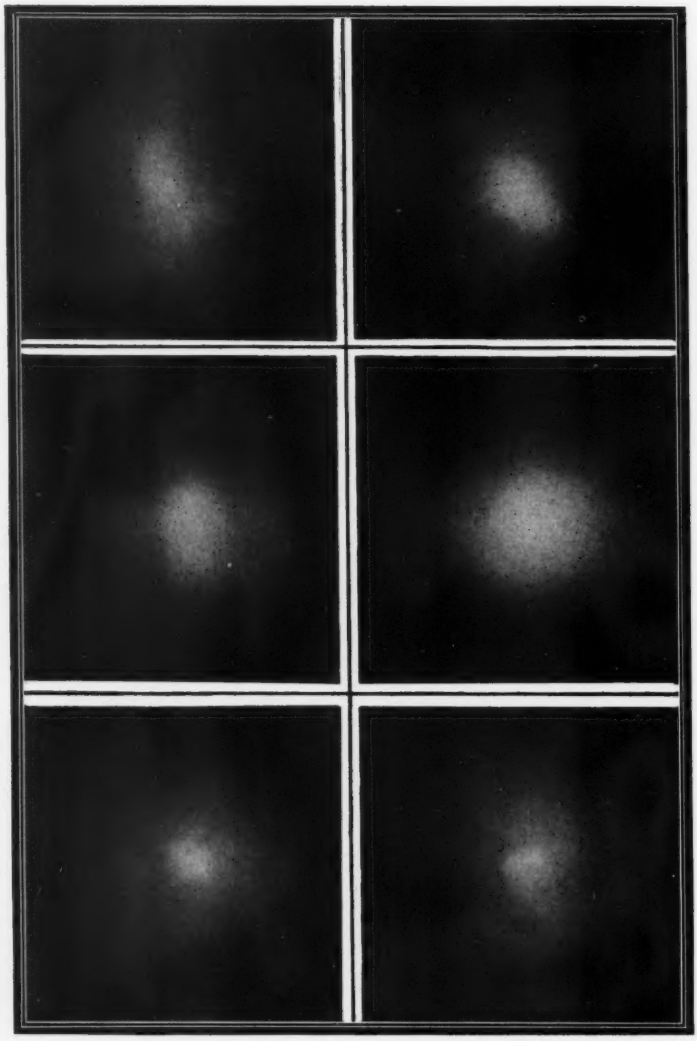
FIG. 16

FIG. 17

FIG. 18

FIG. 19

FIG. 20



The chromatic diffusion halo in cultured pearls.

FIG. 21

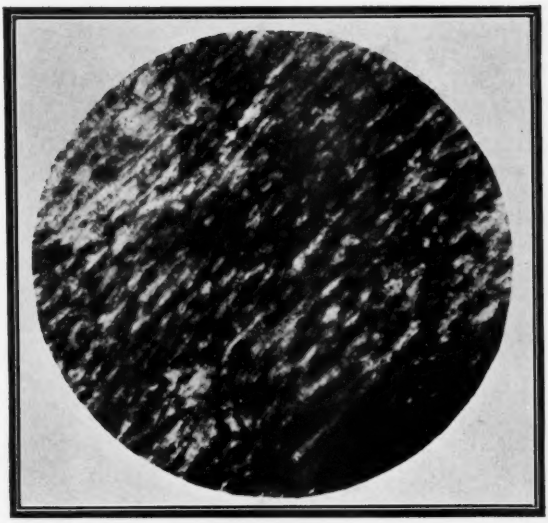


FIG. 22

Illustrating the structure of the material in a cultured pearl.

on any part of the surface to find its way around with relatively small attenuation, thereby making the pearl visible even in regions where no light is directly incident.

7. Summary

The paper discusses the origin and character of the coloured diffusion halo exhibited by pearls surrounding the reflected image of a light source seen at their surface. Twelve photographs illustrative of various types of halo are reproduced. Other aspects of the optical behaviour of pearls are also described and discussed with illustrative photographs.

References

1. Raman, C. V. and Krishnamurti, D. .. *Proc. Ind. Acad. Sci.*, 1954, **39A**, 215.
2. Raman, C. V. .. *Ibid.*, 1935, **1A**, 574.
3. ———— .. *Ibid.*, 1935, **1A**, 859.
4. ——— and Krishnamurti, D. .. *Ibid.*, 1954, **39A**, 1.

ON AN ABSOLUTE CONSTANT IN THE THEORY OF TAUBERIAN SERIES (II)

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1. Introduction

In a previous paper[6] with the same title as this, I obtained an inequality between the partial sums of a series Σa_n of real or complex terms and the Dirichlet-series transform of Σa_n given by

$$F(t)=\Sigma a_n e^{-\lambda_n t},\ t>0,\ 0<\lambda_1<\lambda_2<\ldots,\ \lambda_n\to\infty, \tag{1.1}$$

assuming that, as $n\to\infty$,

$$\frac{a_n\lambda_n}{\lambda_n-\lambda_{n-1}}=O(1),\ \lambda_n-\lambda_{n-1}=O(1).$$

More precisely I proved that, corresponding to a limit point z' of the sequence of partial sums of Σa_n, there is a limit point z'' of $F(t)$ as $t\to+0$ such that

$$|z'-z''|\leqslant\rho\ \limsup_{n\to\infty}\frac{|a_n|\lambda_n}{\lambda_n-\lambda_{n-1}} \tag{1.2}$$

where ρ is a constant whose best (*i.e.*, least) value is

$$\rho_1=\gamma+\log\log 2+2\int_{\log 2}^{\infty}e^{-x}x^{-1}\,dx,\ \gamma=\text{Euler's constant}. \tag{1.3}$$

Previously R. P. Agnew[1] had obtained the above result for the case $\lambda_n=n$ and my treatment of the more general case was, in fact, based on Agnew's work.

In a subsequent paper[7] (Theorem 1) I obtained an inequality exactly like (1.2) between the limit points of

$$A(u)=\int_0^u a(x)\,dx$$

as $u \to \infty$, and those of a certain integral transform

$$F(t) = \int_0^\infty \phi(ut)\, a(u)\, du,\ t > 0,$$

as $t \to +0$, assuming that $ua(u) = O(1)$ as $u \to \infty$. My inequality featured a constant $T(\alpha, 2)$* involving ϕ and a parameter $\alpha > 0$, and having a unique absolute minimum (for $\alpha > 0$) which reduces to the ρ_1 of (1.3) when $\phi(u) = e^{-u}$ and which turns out to be the best possible in the same sense that ρ_1 is the best possible value of ρ in (1.2). This best-possible character of the minimum of $T(\alpha, 2)$ was proved by Agnew who also relaxed some of my conditions on $\phi(u)$ in a later paper.[2] Independently of Agnew's later paper, I had extended the best form of (1.2), with $\rho = \rho_1$, to a series-to-function transform $\Phi_\lambda(t)$ which includes the $F(t)$ of (1.1) and is defined as follows:

$$\Phi_\lambda(t) = \sum_1^\infty a_n \phi(\lambda_n t),\ t > 0,\ 0 < \lambda_1 < \lambda_2 < \ldots,\ \lambda_n \to \infty, \tag{1.4}$$

where $\phi(u)$ is subject to the following standard conditions[5] (pp. 29–30, example (I)):

$$\left.\begin{aligned} \phi(u) &= \int_u^\infty \psi(x)\, dx, \\ \psi(u) \geqslant 0,\ \int_0^\infty \psi(u) \,|\log u|\, du &< \infty,\ \int_0^\infty \psi(u)\, du = 1. \end{aligned}\right\} \tag{1.5}$$

Since my extension to $\Phi_\lambda(t)$, of the best form of (1.2) in which $\rho = \rho_1$ has been merely stated without proof[8] (p. 419) a proof of it is now recorded in order to make my earlier discussion in these *Proceedings*[6] complete.

2. Two Theorems and Lemmas

The extension to the Φ_λ-transform, of (1.2) by itself, without any consideration as to the value of ρ for which it becomes the best possible, is an immediate consequence of the following theorem which H. Delange established[3] (Théorème 4) with conditions on $\phi(u)$ more general than (1.5) and which I derived[8] (§2) from somewhat different considerations applicable also to the Borel transform of a series Σa_n in which $a_n\sqrt{n} = O(1)$ as $n \to \infty$.

Theorem C.—*Let $\Phi_\lambda(t)$ be defined as in* (1.4) *with $\phi(u)$ satisfying* (1.5),

* $T(\alpha, 2)$ is the same as the constant $\tau(\alpha)$ defined in (2.3) of this paper.

Let

$$a_n = O\left(\frac{\lambda_n - \lambda_{n-1}}{\lambda_n}\right), \quad \frac{\lambda_n}{\lambda_{n-1}} \sim 1, \; n \to \infty. \tag{2.1}$$

Then

$$\limsup_{t \to +0} \; | \Phi_\lambda(t) - \sum_{\lambda_n \leqslant \alpha/t} a_n | \leqslant \tau(\alpha) \limsup_{n \to \infty} \frac{| a_n | \lambda_n}{\lambda_n - \lambda_{n-1}} \tag{2.2}$$

where α is positive constant and

$$\tau(\alpha) = \alpha \int_0^\infty \psi(\alpha u) \, | \log u | \, du \equiv \int_0^a \{1 - \phi(u)\} u^{-1} \, du + \int_a^\infty \phi(u) u^{-1} du. \tag{2.3}$$

The conclusion (2.2) *is the best possible on our suppositions since the equality sign in it cannot be omitted.*

Theorem C is, in fact, a generalization of Theorems A, B of the paper[4] (" Postscript ") to which this is a sequel. A simple argument[6] (§3, p. 541) shows that Theorem C includes part (i) of the main result of the present paper:

THEOREM D.—*In Theorem C, suppose that $\alpha_0 > 0$ exists such that*

$$\phi(\alpha_0) = \tfrac{1}{2}, \; \phi(u) > \tfrac{1}{2} \text{ for } 0 < u < \alpha_0, \; \phi(u) < \tfrac{1}{2} \text{ for } u > \alpha_0, \dagger \tag{2.4}$$

this supposition necessarily implying that $\tau(\alpha)$ defined by (2.3) *has a unique absolute minimum τ_0 when $\alpha = \alpha_0$. Let $\mathcal{L}$ denote the set of limit points of $\Sigma_{\lambda_n < x} a_n$ as $x \to \infty$ and $\mathcal{L}_\phi$ the set of limit points of $\Phi_\lambda(t)$ as $t \to +0$.*

Then

(i) *to each $z' \in \mathcal{L}$ corresponds a $z'' \in \mathcal{L}_\phi$ such that*

$$| z' - z'' | \leqslant \tau_0 \limsup_{n \to \infty} \frac{| a_n | \lambda_n}{\lambda_n - \lambda_{n-1}}. \tag{2.5}$$

(ii) *τ_0 in* (2.5) *cannot be replaced by a smaller positive number*, i.e., *more precisely, given $\{\lambda_n\}$ such that $\lambda_n - \lambda_{n-1} \to k > 0$, we can construct a series Σa_n which satisfies the Tauberian condition in* (2.1) *and falsifies* (2.5) *when τ_0 is replaced by $\tau_0 - \epsilon$, ϵ being any small positive number.*

While the proof of Theorem D (i) requires nothing more than Theorem C, that of Theorem D (ii) requires two other results stated below as lemmas. Lemma I is obvious enough to need no proof. Lemma II is borrowed

† A simple condition sufficient for (2.4) is that $\phi(u) > 0$ for $0 \leqslant u < 1$.

from Agnew[2] (pp. 512–14) for the reason that it effects a considerable simplification in the proof of Theorem D (ii)‡.

LEMMA I.—*If $f(x)$ is positive, monotonic decreasing, and if $\{\lambda_n\}$ is the sequence in* (1.4) *subject to the additional condition $\lambda_n - \lambda_{n-1} < K$, then*

$$-Kf(\lambda_N) < \sum_{\nu=N+1}^{n} (\lambda_\nu - \lambda_{\nu-1}) f(\lambda_\nu) - \int_{\lambda_N}^{\lambda_n} f(x)\,dx \leqslant 0\,.$$

LEMMA II.—*Conditions* (1.5) *and the existence of α_0 satisfying* (2.4) *ensure the existence of a λ_0 corresponding to any given $\epsilon_0 > 0$, such that, for $\lambda > \lambda_0$,*

$$\int_{x/\lambda}^{x} \phi(u)\,u^{-1}\,du - \int_{x}^{x\lambda} \phi(u)\,u^{-1}\,du \qquad (x > 0)$$

$$< \epsilon_0 + \log\lambda - \int_{0}^{\alpha_0} \{1-\phi(u)\}\,u^{-1}\,du - \int_{\alpha_0}^{\infty} \phi(u)\,u^{-1}\,du \equiv \epsilon_0 + \log\lambda - \tau_0\,.$$

3. A SPECIAL SERIES AND ITS Φ_λ-TRANSFORM

A special series for use in the proof of Theorem D (ii), very much like another series constructed in the first part of this paper already published[6] (Lemma 5), is discussed in the next lemma.

LEMMA III.—*Let $\{\lambda_n\}$ be a sequence such that*

$$0 < \lambda_1 < \lambda_2 < \ldots,\ \lambda_n \to \infty,\ \lambda_n - \lambda_{n-1} \to k > 0.$$

Let ϵ_0 be an arbitrarily small positive number. Then we can construct a series

$$\left.\begin{aligned} \Sigma a_n(p) \equiv 0 + 0 \ldots 0 + \xi_p + \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \\ - \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + 0 + 0 + \ldots, \\ \xi_p = -\sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \end{aligned}\right\} \qquad (3.1)$$

where

$$p = p(\epsilon_0),\ q = q(\epsilon_0, p, \lambda),\ m = m(\epsilon_0, q, \lambda),\ \lambda = \lambda(\epsilon_0),$$

‡ My original (unpublished) proof of Theorem D (ii), which did not make use of Lemma II was more cumbrous than the proof given in this paper.

p and λ being such that

$$\frac{\lambda_p \mid \xi_p \mid}{\lambda_p - \lambda_{p-1}} < 1 + \epsilon_0, \tag{3.2}$$

$$\sum_{\nu=1}^{n} a_\nu(p) < \log \lambda + 2\epsilon_0 \ (n = 1, 2, \ldots), \ \sum_{\nu=1}^{q} a_\nu(p) > \log \lambda - \epsilon_0, \tag{3.3}$$

and $\Phi(t, p)$, the Φ_λ-transform of $\Sigma a_n(p)$ whose kernel $\phi(u)$ is subject to (1.5) *and* (2.4), *satisfies the inequality*

$$\Phi(t, p) < 7\epsilon_0 + \log \lambda + \tau_0, \ \tau > 0, \tag{3.4}$$

where τ_0 is the constant defined in enunciations of Theorem D and Lemma II.

Proof.—A series $\Sigma a_n(p)$ defined as in (3.1) and satisfying (3.2), (3.3), (3.4) may be obtained as follows. Choose a positive $\epsilon_1 < 1$ such that

$$2\,\frac{\epsilon_1(1 + \epsilon_1)}{1 - \epsilon_1} + \frac{1 + \epsilon_1}{1 - \epsilon_1} < 1 + \epsilon_0. \tag{3.5}$$

Also, choose a positive integer N such that

$$k(1 - \epsilon_1) < \lambda_n - \lambda_{n-1} < k(1 + \epsilon_1) \text{ for } n > N, \tag{3.6}$$

and then $p > N$ such that

$$\lambda_p > 2\,\frac{k}{\epsilon_0} > \frac{k(1 + \epsilon_1)}{\epsilon_0}. \tag{3.7}$$

Next choose $\lambda > 1/\epsilon_1$ such that

$$\int_{a/\lambda}^{a} \phi(u)\, u^{-1}\, du - \int_{a}^{a\lambda} \phi(u)\, u^{-1}\, du < \epsilon_0 + \log \lambda - \tau_0, \tag{3.8}$$

this being possible by Lemma II. Afterwards choose the least integers q, m such that

$$\lambda \leqslant \begin{cases} \dfrac{\lambda_q}{\lambda_p} < \lambda + \dfrac{k(1 + \epsilon_1)}{\lambda_p}, \\ \dfrac{\lambda_m}{\lambda_q} < \lambda + \dfrac{k(1 + \epsilon_1)}{\lambda_q}. \end{cases} \tag{3.9}$$

In the series $\Sigma a_n(p)$ specified in the last paragraph we can use Lemma I for each of the two sums composing ξ_p and write

$$\xi_p = -\int_{\lambda_p}^{\lambda_q} dx/x + I_p + \int_{\lambda_q}^{\lambda_m} dx/x - I_q \tag{3.10}$$

where I_p, I_q are such that

$$|I_p| < \frac{k(1+\epsilon_1)}{\lambda_p}, \quad |I_q| < \frac{k(1+\epsilon_1)}{\lambda_q}.$$

Hence

$$|\xi_p| < \left|\log \frac{\lambda_m/\lambda_q}{\lambda_q/\lambda_p}\right| + |I_p| + |I_q|$$

$$< \log\left\{\left[\lambda + \frac{k(1+\epsilon_1)}{\lambda_p}\right]\Big/\lambda\right\} + \frac{k(1+\epsilon_1)}{\lambda_p} + \frac{k(1+\epsilon_1)}{\lambda_q} \quad (3.11)$$

by (3.9). From (3.11) we get first, using (3.7),

$$|\xi_p| < \frac{k(1+\epsilon_1)}{\lambda\lambda_p} + 2\frac{k(1+\epsilon_1)}{\lambda_p} < 3\frac{k(1+\epsilon_1)}{\lambda_p} < 3\epsilon_0, \quad (3.12)$$

and then, using the fact that $n=p$ satisfies (3.7) and that $\lambda_p/\lambda_q \leqslant 1/\lambda$ by (3.9),

$$\frac{\lambda_p|\xi_p|}{\lambda_p - \lambda_{p-1}} < \frac{k(1+\epsilon_1)}{k\lambda(1-\epsilon_1)} + \frac{k(1+\epsilon_1)}{k(1-\epsilon_1)} + \frac{k(1+\epsilon_1)}{k\lambda(1-\epsilon_1)}.$$

Since $\lambda > 1/\epsilon_1$, the last inequality, taken along with (3.5), gives at once (3.2).

The definition of $\Sigma a_n(p)$ in (3.1) shows that, for all n,

$$\sum_{\nu=1}^{n} a_\nu(p) \leqslant \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} = \int_{\lambda_q}^{\lambda_m} dx/x - I_q$$

in the notation of (3.10). The first part of (3.3) is derived from the above inequality by arguing as in the passage from (3.10) to (3.12); while the second part of (3.3) is obvious from

$$\sum_{\nu=1}^{q} a_\nu(p) = \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} = \int_{\lambda_q}^{\lambda_m} dx/x - I_q \geqslant \log\lambda - |I_q|.$$

To prove (3.4) we start with the definition of $\Phi(t,p)$, $t>0$, *viz.*,

$$\Phi(t,p) = 0 + 0 \ldots 0 + \xi_p\phi(\lambda_p t) + \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu}\phi(\lambda_\nu t)$$

$$- \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu}\phi(\lambda_\nu t) + 0 + 0 + \ldots$$

$$= \xi_p\phi(\lambda_p t) + \int_{\lambda_p}^{\lambda_q} \phi(xt)\, x^{-1}\, dx - J_p - \int_{\lambda_q}^{\lambda_m} \phi(xt)\, x^{-1}\, dx + J_q \text{ (say)} \quad (3.13)$$

where, by Lemma I and (3.7),

$$\left.\begin{aligned} |J_p| &< k(1+\epsilon_1)\frac{\phi(\lambda_p t)}{\lambda_p} < \frac{k(1+\epsilon_1)}{\lambda_p} < \epsilon_0, \\ |J_q| &< k(1+\epsilon_1)\frac{\phi(\lambda_q t)}{\lambda_q} < k(1+\epsilon_1)\frac{\phi(\lambda_p t)}{\lambda_p} < \epsilon_0. \end{aligned}\right\} \tag{3.14}$$

From (3.13) we get

$$\Phi(t,p) < |\xi_p| + \int_{\lambda_p t}^{\lambda_q t} \phi(u)\, u^{-1}\, du - \int_{\lambda_q t}^{\lambda_m t} \phi(u)\, u^{-1}\, du + |J_p| + |J_q$$

which gives, when we put $\lambda_q t = x$ and use (3.12), (3.14),

$$\Phi(t,p) < 5\epsilon_0 + \int_{(\lambda_p/\lambda_q)x}^{x} \phi(u)\, u^{-1}\, du - \int_{x}^{(\lambda_m/\lambda_q)x} \phi(u)\, u^{-1}\, du$$

$$< 5\epsilon_0 + \int_{x/\Lambda}^{x} \phi(u)\, u^{-1}\, du - \int_{x}^{x\lambda} \phi(u)\, u^{-1}\, du, \quad \Lambda = \lambda + \frac{k(1+\epsilon_1)}{\lambda_p},$$

by (3.9). Hence

$$\Phi(t,p) < 5\epsilon_0 + \int_{x/\Lambda}^{x/\lambda} \phi(u)\, u^{-1}\, du + \left\{ \int_{x/\lambda}^{x} \phi(u)\, u^{-1}\, du - \int_{x}^{x\lambda} \phi(u)\, u^{-1} du \right\}. \tag{3.15}$$

An upper estimate for the second term on the right side of (3.15) is

$$\log \frac{\Lambda}{\lambda} = \log\left[1 + \frac{k(1+\epsilon_1)}{\lambda\lambda_p}\right] < \epsilon_0$$

as in (3.12); while an upper estimate for the third term (in flower brackets) on the right side of (3.15) is, by (3.8),

$$\epsilon_0 + \log\lambda - \tau_0.$$

Using the above two upper estimates in (3.15), we get at once (3.4) and conclude the proof of Lemma III.

4. Proof of Theorem D

After Theorem C, part (i) of Theorem D needs no proof as already stated.

To prove part (ii) of Theorem D we proceed in this wise. We obtain a series Σa_n by the termwise addition of series $\Sigma a_n(p_1)$, $\Sigma a_n(p_2)$, ..., all of the type of $\Sigma a_n(p)$ in (3.1). If the sequence of positive integers p_r, $r = 1, 2, \ldots$, is increasing and such that the series $\Sigma a_n(p_r)$ do not overlap

when added termwise, the series got by addition will plainly satisfy the following two conditions. First, on account of the restriction on ξ_{p_r} similar to (3.2),

$$\limsup \frac{|a_n|\lambda_n}{\lambda_n - \lambda_{n-1}} = 1.$$

Secondly, since

$$\sum_{\nu=1}^{n} a_\nu = \sum_{\nu=1}^{n} a_\nu (p_{r-1}),\ p_{r-1} \leqq n < p_r,$$

it follows from (3.3) that

$$\limsup \sum_{\nu=1}^{n} a_\nu = \log \lambda.$$

If further $\{p_r\}$ can be chosen so that $\Phi(t)$, representing the Φ_λ-transform of Σa_n, satisfies the inequality

$$\Phi(t) < \epsilon + \log \lambda - \tau_0,\quad 0 < t \leqq t_1, \tag{4.1}$$

for any small $\epsilon > 0$, it will follow that the series Σa_n falsifies (2.5) when τ_0 is replaced $\tau_0 - \epsilon$ and the proof of Theorem D (ii) will be complete.

A choice of $\{p_r\}$ satisfying these requirements may be made as follows. Corresponding to the given $\epsilon > 0$, we first choose ϵ_0 so that

$$\epsilon_0 (9 + \epsilon_0) < \epsilon, \tag{4.2}$$

and then ϵ_1, p, λ as in (3.5), (3.7), (3.8) respectively, thus determining $\Sigma a_n(p)$. We take $p_1 = p$ and then find t_1 so that

$$|\Phi(t, p_1)| < \epsilon_0 \text{ for } t \leqq t_1,$$

this being possible since $\Phi(t, p_1) \to 0$ as $t \to +0$. We next choose p_2 so that

$$\lambda_{p_2} > \Lambda^2 \lambda_{p_1},\ \Lambda = \lambda + \frac{k(1+\epsilon_1)}{\lambda_{p_1}},$$

thus ensuring that the series $\Sigma a_n(p_1)$, $\Sigma a_n(p_2)$ do not overlap when added termwise. The choice of p_r for $r \geqq 3$ and of t_r for $r \geqq 2$ may now be defined inductively as follows. After choosing $p_1, p_2, \ldots p_{r-1}$ and $t_1, t_2, \ldots t_{r-2}$ $(r \geqq 3)$, we choose first t_{r-1} and then p_r so that

$$\sum_{j=1}^{r-1} |\Phi(t, p_j)| < \epsilon_0 \text{ for } t \leqq t_{r-1}, \tag{4.3}$$

$$\lambda_{p_r} > \Lambda^2 \lambda_{p_{r-1}}, \tag{4.4}$$

$$\int_{t_{r-1}\lambda_{-1+p_r}}^{\infty} \phi(u)\, u^{-1}\, du < \epsilon_0. \tag{4.5}$$

A choice of t_{r-1} and p_r as in (4.3) and (4.4) is clearly possible, while a choice of p_r so as to satisfy additionally (4.5) is rendered possible by the convergence at ∞ of the integral in (4.5).

Having chosen $\{p_r\}$ and $\{t_r\}$ as in the preceding paragraph, we proceed to consider, for $t_r < t \leqslant t_{r-1}$, $r \geqslant 2$,

$$\Phi(t) = \sum_{j=1}^{r-1} \Phi(t, p_j) + \Phi(t, p_r) + \sum_{j=r+1}^{\infty} \Phi(t, p_j).$$

By the condition on ξ_{p_j}, $j \geqslant r+1$, similar to (3.2) and the condition obviously satisfied by the other terms of Σa_n, we obtain from the last step

$$\Phi(t) < \sum_{j=1}^{r-1} |\Phi(t, p_j)| + \Phi(t, p_r) + (1+\epsilon_0) \sum_{\nu=p_{r+1}}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \phi(\lambda_\nu t). \quad (4.6)$$

Now

$$0 < \sum_{\nu=p_{r+1}}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \phi(\lambda_\nu t) < \int_{\lambda_{-1}+p_{r+1}}^{\infty} \phi(xt)\, x^{-1}\, dx = \int_{t\lambda_{-1}+p_{r+1}}^{\infty} \phi(u)\, u^{-1}\, du$$

$$< \int_{t_r\lambda_{-1}+p_{r+1}}^{\infty} \phi(u)\, u^{-1}\, du < \epsilon_0 \quad (4.7)$$

by (4.5). Using (4.3) in the first term of (4.6), (3.4) in the second term and (4.7) in the third term, we get

$$\Phi(t) < \epsilon_0(9+\epsilon_0) + \log\lambda - \tau_0, \quad t_r < t \leqslant t_{r-1}\ (r \geqslant 2). \quad (4.8)$$

(4.8), taken along with (4.2), gives (4.1) and so completes the proof of Theorem D (ii).

5. The Tauberian Constants for some Special Φ_λ-Transforms

Theorems C, D are applicable to the following cases of the kernel $\psi(u)$ each of which defines a familiar method of summability whose name is indicated in brackets.

(1) $\psi(u) = k(1-u)^{k-1}$ for $0 \leqslant u < 1$, 0 for $u > 1$, where $k > 0$ (Riesz).

(2) $\psi(u) = e^{-u}$ (Laplace-Abel).

(3) $\psi(u) = \dfrac{k}{(1+u)^{k+1}}$ where $k > 0$ (Stieltjes).

(4) $\psi(u) = -\dfrac{d}{du}\left(\dfrac{u}{e^u - 1}\right)$ for $u > 0$ (Lambert).

(5) $\psi(u) = \dfrac{2}{\pi}\dfrac{\sin^2 u}{u^2}$ for $u > 0$ (R_2 or Riemann second-order).

If the values of τ_0 corresponding to (1), (2), (3) above are denoted by $\tau_0(R, k)$, $\tau_0(A)$, $\tau_0(S, k)$ respectively then, as $k \to \infty$,

(i) $\tau_0(R, k) \uparrow \tau_0(A)$, (ii) $\tau_0(S, k) \downarrow \tau_0(A)$.

(i) follows from considerations first put forward by Garten in a similar context[4] (pp. 323–24). (ii) is an observation due to Agnew[2] (p. 505).

References

1. Agnew, R. P. .. "Abel transforms of Tauberian series," *Duke Math. J.*, 1945, **12**, 27–36.
2. ———— .. "Integral transformations and Tauberian constants," *Trans. Amer. Math. Soc.*, 1952, **72**, 501–18.
3. Delange, H. .. "Sur les théorèmes inverses des procédés de sommation des séries divergentes (Premier Mémoire)," *Ann. Sci. École. Norm. Sup.* (3), 1950, **67**, 99–160.
4. Garten, V. .. "Uber Taubersche Konstanten bei Cesàroschen Mittelbildungen," *Comment. Math. Helv.*, 1951, **25**, 311–35.
5. Karamata, J. .. *Sur les théorèmes inverses des procédés de sommabilitié*, 1937, (Act. sci. industr. No. **450**, VI).
6. Rajagopal, C. T. .. "On an absolute constant in Tauberian theory," *Proc. Ind. Acad. Sci.*, 1948, **28A**, 537–44.
   "Postscript," *Ibid.*, 1950, **31A**, 60–61.
7. ———— .. "On a generalization of Tauber's theorem," *Comment. Math. Helv.*, 1950, **24**, 219–31.
8. ———— .. "A generalization of Tauber's theorem and some Tauberin constants," *Math. Z.*, 1953, **57**, 405–14.

BEHAVIOUR OF SURFACE ACTIVE SUBSTANCES AT THE DROPPING MERCURY ELECTRODE AT DIFFERENT FREQUENCIES OF THE APPLIED FIELD

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Introduction

While studying the effect of surface active substances on the kinetics of discharge of metallic ions at the dropping mercury electrode in pulsating fields[1] it was observed that the velocity of discharge was greatly brought down by the presence of such substances as gelatine. An elegant technique based on measurement of phase difference has been used by Randles[2] who has reported that addition of gelatine brought down the rate of discharge of cadmium ion by a thousand times. Keilin has also made a similar observation in polarographic measurements.[3] This has been attributed to the surface active substance getting adsorbed at the mercury surface and hindering the electrode processes in the covered areas. The adsorption of surface active substances is also known to lower the capacity of the electric double layer and is often responsible for low values of capacity reported in literature.[4] From the point of view of studying the adsorbability of surface active substances at mercury-aqueous interfaces, it would be better to investigate the latter phenomenon as the number of complicating factors is smaller and the results would be easier to interpret.

The first detailed investigation of the effect of surface active substances on the capacity of the dropping mercury electrode was made by Proskurnin and Frumkin.[5] Their experiments showed the existence of two maxima with a strong depression in the middle part in the capacity potential curve of sodium sulphate saturated with octyl alcohol. These features were confirmed by the more precise measurements of Grahame.[6] The pulsating field technique[5] as modified in this laboratory is found to be very convenient for the investigation of these phenomena.[7] Breyer and Hacobian have also used a similar technique for such investigations.[8] Interesting results have been obtained with regard to the behaviour of bromocresol purple at the mercury-aqueous interfaces.[9, 10] The present work relates to the effect of

the frequency of the a.c. ripple on the behaviour of the surface active substances at the dropping mercury electrode.

Experimental

Materials used.—1. Isobutyl alcohol was Merck's purest quality, redistilled twice in an all-glass apparatus collecting the fraction boiling from 106°–108° C.

2. Lauryl-*p*-toluidine-2-sodium sulphonate was a purified sample kindly prepared and supplied by Dr. K. Venkatraman, Director, Department of Chemical Technology, Bombay University.

3. The mercury used for the dropping and the pool electrodes was purified by passing several times through Meyer's column, washed with distilled water, dried and passed through a sintered glass filter.

4. The other chemicals used were of 'Analar' quality of B.D.H.

Technique of measurement.—The technique (Fig. 2) consists in applying to the dropping mercury electrode a 45 mv. (r.m.s.) a.c. ripple of the required frequency over the d.c. potential and observing the alternating component of the resulting pulsating current. The B.S.R. oscillator of (B.S.R. Ltd., Berks, England) was used as the source of the alternating current. The frequency could be adjusted to any desired value. It was found, however, that the output voltage of the oscillator was fluctuating rather too much. To avoid this, the output of the oscillator was fed into a multipurpose amplifier fabricated as per our specifications by the Central India Radio, Kanpur, the line diagram of which is given in Fig. 1. The amplifier gain was adjusted to get an output of 220 volts. This was passed through a mains resistance and a current regulator lamp. The potential drop across the mains resistance was thus maintained constant within one per cent. and had a good wave form. The a.c. ripple was obtained from this by a suitable potentiometric arrangement.

Normally the experiments were done employing the series circuit as shown in Fig. 2. With a view to see if the reduction of the resistance of the system has any effect on the behaviour, an experiment was conducted with the a.c. ripple applied to the dropping mercury electrode by a parallel arrangement as shown in Fig. 3. The required d.c. voltage obtained from the potentiometer A was applied between the dropping mercury electrode D and the pool electrode P. The heavy inductance I helped to prevent the a.c. passing through the d.c. potentiometer. The a.c. ripple obtained by the arrangement described earlier was applied between D and P. The condenser C helped to prevent the draw of the d.c. current from the system

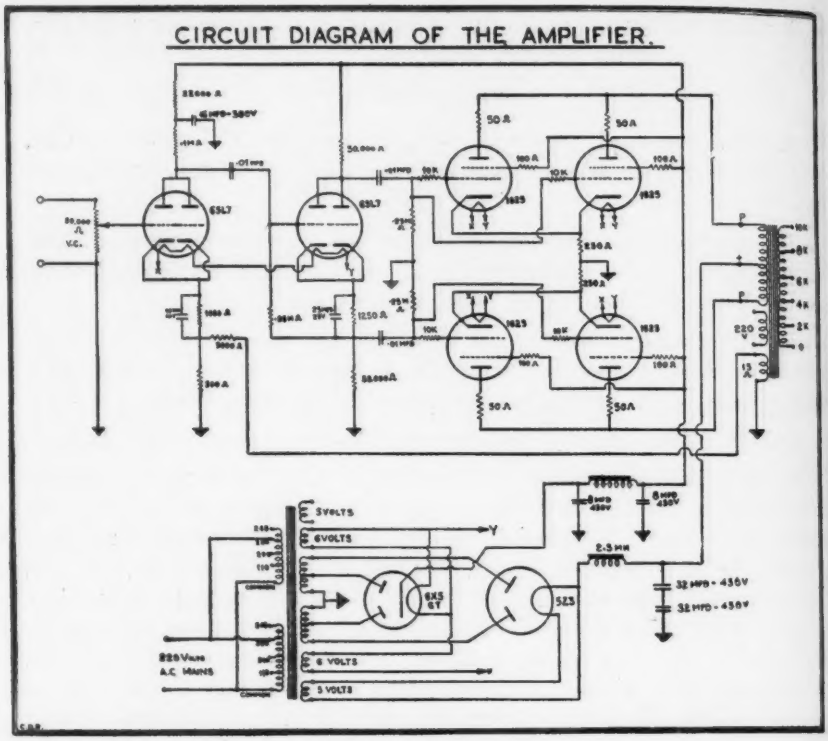

FIG. 1.

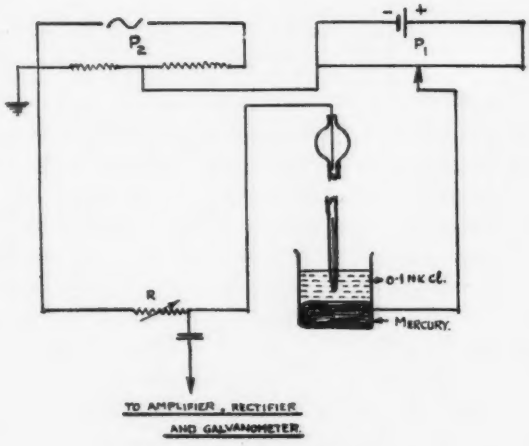

FIG. 2. Series Circuit

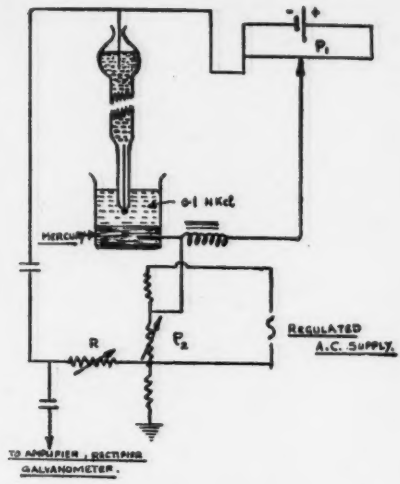

FIG. 3. Parallel Circuit

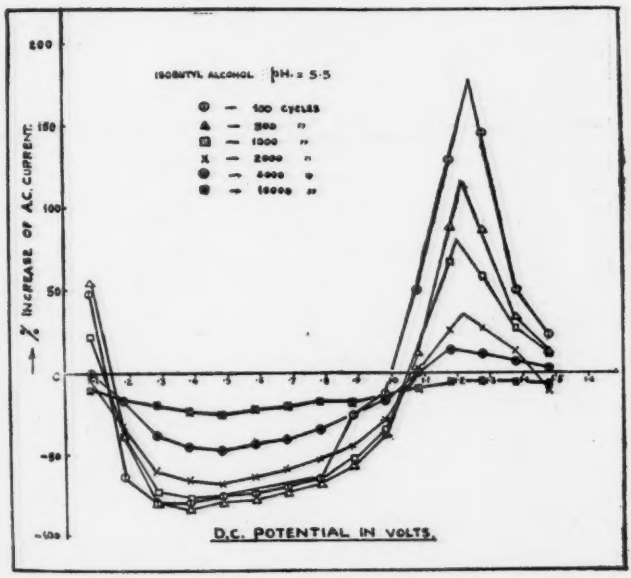

FIG. 4.

through the a.c. circuit. The d.c. potentials between the dropping mercury electrode and the pool electrode were measured in every case directly

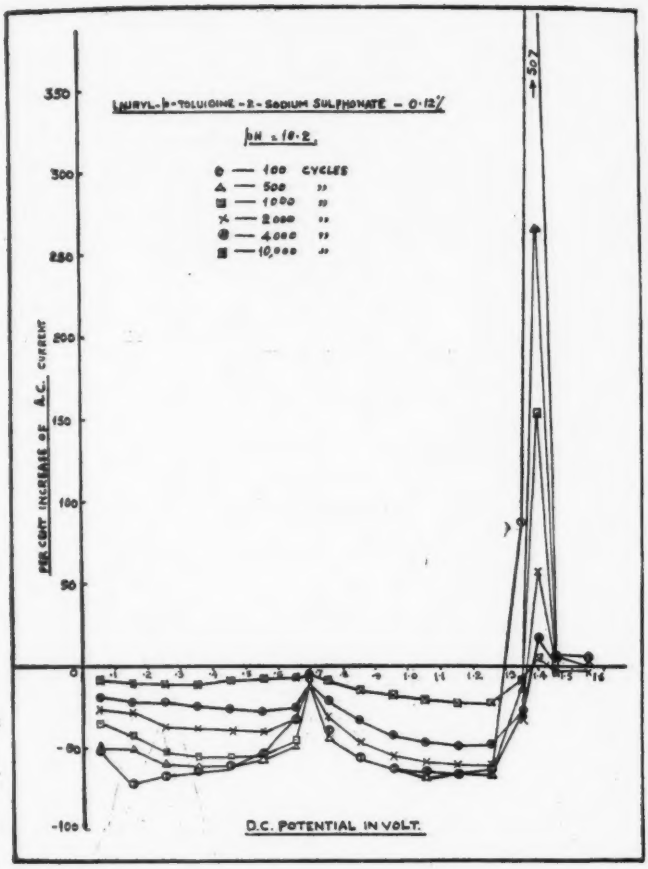

FIG. 5.

by means of a d.c. potentiometer. The potential of the pool electrode was also measured with reference to the saturated calomel electrode. The d.c. potentials of the dropping mercury electrode were then calculated as referred to the saturated calomel electrode and these values have been used for plotting in the graph. Decinormal potassium chloride solution was used as the indifferent electrolyte.

The behaviour of isobutyl alcohol is shown in Fig. 4. The behaviour of lauryl-*p*-toluidine-2-sodium sulphonate is shown in Figs. 5 and 6, the former gives the results obtained by the usual series circuit arrangement

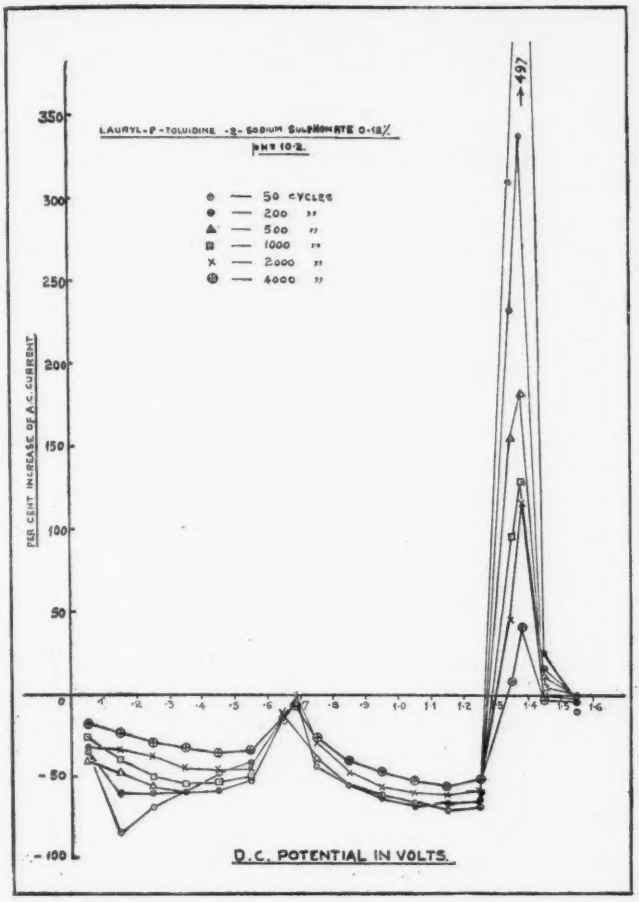

FIG. 6.

and the latter by the parallel circuit arrangement, described in this paper (Fig. 4).

DISCUSSION

A. *General features.*—An examination of Fig. 4 shows that isobutyl alcohol shows as usual a maximum depression of the dropping mercury electrode capacity in the neighbourhood of the electrocapillary zero. At a potential of about 1·2 volts the desorption peak develops. There is a clear indication of the development of another desorption peak on the anodic side of the electrocapillary zero as well,

Lauryl-*p*-toluidine-2-sodium sulphonate shows a similar depressing effect on capacity near the electrocapillary zero. At more cathodic potentials there are two desorption peaks exhibited. The first of them occurs at potentials at which the depression of the capacity is yet very effective and even at potentials very close to the peak the per cent. Δ_i is negative. This novel behaviour indicates a considerable change in amount of adsorption with potential; but the change is attended by relatively small transfer of electric charge across the interface. The second desorption peak occurring at still higher cathodic potentials (1·35 V) is a peak of unusually high magnitude reminding one of a reduction peak corresponding to a polarographic wave. This is not a reduction peak as this compound has no easily reducible group responding polarographically at this potential. The peak is not caused by any delayed reduction of oxygen, as the de-aerated solution shows nearly the same magnitude of the peak. The unusually high magnitude of this desorption peak is therefore presumably caused amongst other factors by the ionised end group bringing about large changes in the distribution of ions during sorption and desorption.

B. *Effect of frequency.*—One interesting feature is that the depression of the capacity due to adsorption at 0·5 volts d.c. is nearly independent of frequency from 50 to 1,000 cycles in both the systems studied. Any further increase in frequency decreases the depression of capacity due to adsorption. This behaviour indicates that *whereas the adsorption film effectively hinders electrode processes that give rise to the condenser current at low frequencies, the film does not appear to have any considerable deterrent action on the passage of the high frequency current.* This new fact is of profound significance and extension of these studies to other systems is likely to reveal the mechanism of the condenser current.

The increase of frequency is found to lower the main desorption peaks in both the systems examined (Figs. 4 and 5). It is to be noted that the per cent. increase of a.c. has been plotted and hence is of great significance. It may be recalled that the technique of measurement is such that the change of frequency does not introduce any error in the measurement.[11] It is, however, possible that at very high capacities and frequencies the resistive impedence of the system may become an important of the total impedance and influence the results. This was confirmed by the experiments using a parallel circuit (Fig. 4), involving very low resistive impedence, which gave higher peaks at the high frequencies (Fig. 6). The general behaviour however was reproduced by the parallel circuit as well, showing a decrease of the magnitude of the main desorption peaks with increase in frequency.

This amazing feature is revealing and shows that there are certain slow processes contributing towards passage of electric charge through the interface during sorption and desorption cycles. It may be that the sorption and desorption processes themselves may take time or it may be that the other attendant processes such as distribution of ions may be slow. This is a matter for further investigation.

Summary

Increase in frequency is found to lower the depressing effect of the adsorption films of surface active substances on the dropping mercury electrode capacity. This fact appears to be of great interest from the point of view of elucidating the factors controlling the condenser current. Increase in frequency decreases the desorption peaks which points at the existence of some slow processes controlling the passage of electric charges during the sorption and desorption cycles.

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References

1. Kalyanasundaram and Tandon .. Unpublished.
2. Randles .. *Faraday Soc. Discussion*, 1947, **1**, 11.
3. Keilin .. *J. Am. Chem. Soc.*, 1948, **70**, 1984.
4. (*a*) Breyer and Gutman .. *Faraday Soc. Discussion*, 1947, **1**, 25.
   (*b*) *cf.* Ershler .. *Ibid.*, 1947; **1**, 48.
   (*c*) *cf.* Bowden and Grew .. *Ibid.*, 1947, **1**, 49.
5. Proskurnin and Frumkin . *Trans. Far. Soc.*, 1935, **31**, 110.
6. Grahame .. *Am. Chem. Soc.*, 1946, **68**, 301.
7. Doss and Kalyanasundaram .. *Proc. Ind. Acad. Sci.*, 1952, **35**, 27.
8. Breyer and Hacobion .. *Australian J. of Scientific Research*, Series A, 1952, **5**, 500.
9. Doss and Gupta .. *Proc. Ind. Acad. Sci.*, 1952, **36**, 493.
10. Gupta .. *J. Sci. and Ind. Res.*, 1953, **12B**, 84.
11. Doss and Kalyanasundaram .. *Proc. Ind. Acad. Sci.*, 1951, **33**, 298.

THE TEMPERATURE VARIATION OF THE ROTATORY POWER OF QUARTZ FROM 30° TO 410° C.

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It has long been known that the rotatory power of quartz increases when the temperature of the crystal is raised (Soleil, 1845; Dubrunfaut, 1846). Numerous investigations dealing with this effect are on record, and these have been reviewed in detail by Sosman in his treatise on the properties of silica (*A.C.S.*, 1927, pp. 688–97). Measurements are available over a wide range of temperatures, from $-180°$ to 900° C., but no attempt appears to have been made to give a theoretical explanation of the phenomenon.

In an earlier paper (1952) the present author had shown that the rotatory dispersion of quartz is accurately represented from the visible to the extreme ultraviolet by a simple formula involving only two constants, *viz.*,

$$\rho = k\lambda^2/(\lambda^2 - \lambda_0^2)^2 \tag{1}$$

where $k = 7{\cdot}186$ and $\lambda_0 = 0{\cdot}0926283\,\mu$. The above formula is also expressible in the form

$$\rho = a\nu^2/(\nu_0^2 - \nu^2)^2 \tag{2}$$

where $\nu = 1/\lambda$ and $a = k/\lambda_0^4$. Taking 'a' to be constant but ν_0 to vary with the temperature, we get on differentiating (2)

$$\frac{d\rho}{dt} = \frac{4a\nu^2\nu_0^2}{(\nu_0^2 - \nu^2)^3}\chi_0 = \frac{4k\lambda^4}{(\lambda^2 - \lambda_0^2)^3}\chi_0 \tag{3}$$

where

$$\chi_0 = -\frac{1}{\nu_0}\frac{d\nu_0}{dt} = \frac{1}{\lambda_0}\frac{d\lambda_0}{dt}.$$

Hence, the temperature coefficient

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{4\lambda^2}{(\lambda^2 - \lambda_0^2)}\chi_0 \tag{4}$$

It was shown earlier (*loc. cit.*) that the temperature variation of the rotatory power was calculable on the basis of (3), the rate of shift of the characteristic frequency with temperature being found to be roughly the same as that

estimated from the thermal variation of the refractive indices of quartz. However, the available data are inadequate for a complete verification of the theory. From (4), it will be seen that one of the consequences of the theory is that the temperature coefficient should exhibit an increase with decrease of wavelength. Soret and Sarasin (1878) have reported a slight increase in the temperature coefficient in the ultraviolet, a fact which appears to be supported by Molby's observations (1910). But a series of measurements extending over a wider range of wavelengths is necessary before we can arrive at any definite conclusion regarding this matter.

In the present work, the thermal variation of the rotatory power of quartz has been measured from 30° to 410° C. for a range of wavelengths extending from about 6000 Å to 2500 Å. It is shown that the theoretical calculations agree very well with the observational data. The temperature coefficient is found to increase with decrease of wavelength, a fact which is also to be expected from the theory.

2. Experimental Details

Two rods of quartz, cut perpendicular to the optic axis and of fairly good optical quality were used for these experiments. By measuring their rotatory powers at room temperature for a few wavelengths they were tested to be homogeneous and untwinned. The length of the rods were 90·02 mm. and 41·05 mm. respectively.

The quartz crystal selected for the measurement was first wrapped up completely by a thin copper foil (except for two small apertures at the two ends to allow for the passage of light), so as to eliminate any possible variations of temperature along its length. A layer of asbestos was wrapped around the copper foil and the crystal was pushed into a thin-walled porcelain tube whose length was about two or three times the length of the quartz. Nichrome wire of suitable gauge was wound on the outer wall of the tube. By passing a current through this coil, the crystal could be heated to any desired degree. A calibrated thermocouple inserted between the copper foil and the asbestos served to measure the temperature of the crystal. The spectropolarimetric arrangement and the method of procedure were the same as described in Section 2 (*c*) of an earlier paper on the redetermination of the rotatory dispersion of sodium chlorate (1953). The positions of extinctions of the different spectral lines were measured first for the room temperature and then for the higher temperatures. The differences in the rotations could be read off directly for several wavelengths from 5800 Å to 2536 Å. In order to have large increases of rotation, so that the accuracy of experiment may not be too low, measurements were not made at very small intervals of

temperature. With the larger specimen, it was possible to go only upto 200° C. as it unfortunately developed cracks at higher temperatures. But with the smaller specimen, the readings were extended upto about 410° C. The values of $d\rho/dt$ obtained with the two specimens for the different temperature ranges are tabulated below. The data obtained with the bigger specimen are more accurate on account of the larger increases in rotation. As is the convention generally adopted (Sosman, *loc. cit.*), the values of the rotatory power at all temperatures are expressed in terms of the thickness at room temperature. Throughout ρ is expressed in degrees per mm. and λ in microns.

TABLE I

λ	Specimen I Thickness 90·02 mm.		Specimen II Thickness 41·05 mm.			
	31° to 185° C.		28° to 199° C.		199° to 410° C.	
	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$
·2536	380	27·4	200	28·5	300	34·6
·2652	340	24·5	180	25·6	270	31·2
·2753	..	..	..	..	239	27·6
·2804	295	21·3	150	21·4	230	26·6
·2894	260	18·8	137	19·5	210	24·2
·2967	247	17·8	125	17·8	200	23·1
·3022	235	17·0	121	17·2	188	21·7
·3126	210	15·1	110	15·7	170	19·6
·3340	180	13·0	96·5	13·7	141	16·3
·3650	143	10·3	76	10·8	112·5	13·0
·4046	111·5	8·0	60	8·5	86·5 (199–406° C.)	10·2
·4358	97·5	7·0	50	7·1	75 (199–406° C.)	8·8
·5461	55·5	4·0	31·5	4·5	42·5 (199–406° C.)	5·0
·5790	50	3·6	27·5	3·9	37·5 (199–406° C.)	4·4

The temperature coefficient τ may be defined as $\frac{1}{\rho_0}\frac{\Delta\rho}{\Delta t}$ where ρ_0 is the rotatory power at room temperature. For the range 31° to 185° C. we get

for λ 5790, $\tau = 160 \times 10^{-6}$

for λ 2536, $\tau = 184 \times 10^{-6}$

The present value for λ 5790 compares favourably with Gumlich's value of 154×10^{-6} for the range 15° to 174° C. and Le Chatelier's value of 163×10^{-6} for the range 20° to 280° C. (Sosman, *loc. cit.*). Also it will be seen that *the temperature coefficient exhibits an increase with decrease of wavelength.* As has already been pointed out, this is to be expected from (4).

3. Theoretical Calculation

Substituting for k and λ_0 and giving a suitable value for χ_0 in equation (3), the values of $\frac{d\rho}{dt}$ have been calculated for the different wavelengths and for different temperatures. These are given together with the experimental values in Table II. The agreement can be seen to be very satisfactory.

Table II

λ	$d\rho/dt \times 10^3$					
	31° to 185° C.		28° to 199° C.		199° to 410° C.	
	Expt.	Theor. $\chi_1 = 4{\cdot}0 \times 10^{-5}$	Expt.	Theor. $\chi_0 = 4{\cdot}13 \times 10^{-5}$	Expt.	Theor. $\chi_0 = 5{\cdot}05 \times 10^{-5}$
·2536	27·4	27·5	28·5	28·4	34·6	34·7
·2652	24·5	24·2	25·6	24·9	31·2	30·5
·2753	..	..	..	..	27·6	27·5
·2804	21·3	20·7	21·4	21·4	26·6	26·1
·2894	18·8	19·0	19·5	19·6	24·2	24·0
·2967	17·8	17·8	17·8	18·3	23·1	22·4
·3022	17·0	16·9	17·2	17·5	21·7	21·4
·3126	15·1	15·5	15·7	16·0	19·6	19·6
·3340	13·0	13·1	13·7	13·5	16·3	16·5
·3650	10·3	10·5	10·8	10·9	13·0	13·3
·4046	8·0	8·3	8·5	8·5	10·2	10·4
·4358	7·0	7·0	7·1	7·2	8·8	8·8
·5461	4·0	4·2	4·5	4·3	5·0	5·3
·5790	3·6	3·7	3·9	3·8	4·4	4·7

Molby (*loc. cit.*) has measured the rotatory power both at liquid air temperature and at room temperature over the entire visible spectrum. The temperature coefficient for this range has been calculated earlier (*loc. cit.*)

in the same manner using equation (3). The value of χ_c is found to be much less for this range on account of the diminution of the temperature. In general χ_0 increases with rise of temperature as will be evident from Table III.

TABLE III

Temperature Range	$\chi_0 \times 10^5$
−188° to 20°	2·7
31° to 185°	4·0
199° to 410°	5·05

The value of χ obtained in the present calculation is roughly the same as that estimated from the thermal variation of the refraction of quartz and increases in the same manner with rise of temperature (author, *loc. cit.*). Considering that the temperature coefficient of the rotatory power is nearly thirty times the coefficient of the refractive index for λ 5893 Å and that the various dispersion frequencies and their strengths are not uniquely known, this agreement should be considered as excellent.

In the derivation of (3) we have considered 'a' to be invariable with temperature. This assumption is not altogether unjustifiable. Except for the oscillator strength, the quantity 'a' is purely dependent on the changes in volume of the crystal. Numerous experiments on the stress-optical effects in quartz have shown that the rotatory power remains unaltered at all pressures, thus indicating that it is insensitive to changes of volume (Sosman, *loc. cit.*, pp. 768–70). The oscillator strength is also constant with temperature, at least to a first approximation, for, Ramachandran (1947) has shown in a series of papers dealing with the theory of thermal variation of the refractive indices of solids that the numerical calculations are in quantitative accord with the experimental data only on this basis. Therefore, we may without sensible error assume 'a' to be unaltered with temperature. The only way then to explain the temperature variation of the rotatory power is by assuming that ν_0 shifts with temperature, and we have just seen that there is enough evidence in support of this idea.

The author's best thanks are due to Prof. Sir C. V. Raman for the keen and encouraging interest he took in this investigation.

4. SUMMARY

The temperature variation of the rotatory power of quartz has been measured from 30° to 410° C. for a range of wavelengths extending from

6000 Å to 2500 Å. It is found that the temperature coefficient $\left(\frac{1}{\rho_0}\frac{\Delta\rho}{\Delta t}\right)$ exhibits an increase in the ultraviolet. The rotatory dispersion of quartz is accurately expressible from the visible to the extreme ultraviolet by a formula of the form $\rho = a\nu^2/(\nu_0^2 - \nu^2)^2$, where $\nu = \frac{1}{\lambda}$. Taking 'a' to be invariable with temperature (for which reasons have been put forward) but ν_0 to vary with it, the thermal variation of the rotatory power has been calculated over the whole range of wavelengths for the different temperatures. The theoretical calculation agrees very well with the observational data, the rate of shift of ν_0 being found to be roughly the same as that estimated from the thermal variation of the refraction. It is shown that theoretically we should expect the temperature coefficient to increase with decrease of wavelength, a fact which is confirmed by experiment.

References

Chandrasekhar, S. .. *Proc. Ind. Acad. Sci.*, 1952, **35**, 103; 1953, **37**, 458.

Dubrunfaut .. *Comp. Rend.*, 1846, **23**, 44.

Molby, F. A. .. *Phys. Rev.*, 1910, **31**, 291.

Radhakrishnan, T. .. *Proc. Ind. Acad. Sci.*, 1947, **25**, 382.

Ramachandran, G. N. .. *Ibid.*, 1947, **25**, 266; 280; 286; 375; 481: 498.

Soleil .. *Comp. Rend.*, 1845, **20**, 435.

Soret and Sarasin .. *Arch. Sc. Phys. Nat.*, 1882, **8**, 5; 97; 201.

Sosman .. *The Properties of Silica, A.C.S.*, Monographs, 1927.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XLVII. A New Synthesis of 3-Hydroxy Primetin Derivatives

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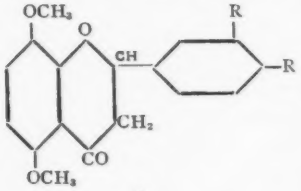
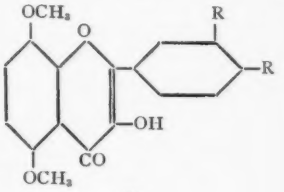
Three-Hydroxy primetin was prepared earlier by Seshadri *et al.*[1] by nuclear oxidation using 3-methoxy-5-hydroxy flavone. In view of the recent simplification in the preparation of 2-hydroxy-3 : 6-dimethoxy acetophenone,[2] the alternative method using this ketone as the starting point has now been adopted. Condensation with benzaldehyde to yield the corresponding chalkone has already been reported by Ballio and Pocchiari.[3] The chalkone has now been converted into the corresponding flavanone (I *a*) and finally into the dimethoxy flavonol (II *a*) using a modification[4] of the method of Kostanecki. The trimethoxy flavone (III *a*) obtained on methylation agrees with the sample prepared earlier.[1] As a useful reference compound for analytical study in this series, alkali fission of the trimethoxy flavone (III *a*) has been carried out and the properties of 2-hydroxy-ω : 3 : 6-trimethoxy acetophenone (IV) recorded.

Using veratraldehyde in the above series of condensations 3 : 5 : 8 : 3′ : 4′ pentamethoxy flavone (III *b*) and the corresponding pentahydroxy flavone have also been prepared. The same pentamethyl ether is obtained by the

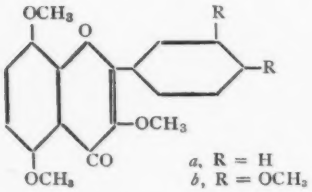


I

a, R = H
b, R = OCH_3

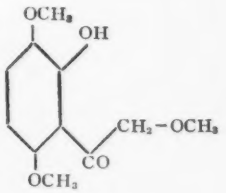


II



a, R = H
b, R = OCH_3

III



IV

condensation of the fission ketone (IV) with the anhydride and sodium salt of veratric acid (Allan-Robinson condensation). That there is no isomeric change during the demethylation of the flavonol methyl ether (II *b*) by means of hydriodic acid has also been proved by the remethylation of the penta-hydroxy flavone whereby the same pentamethoxy flavone (III *b*) is again formed. A similar report was made earlier in the preparation of 3-hydroxy primetin.[1]

Recently Kurth and Hubbard[5] isolated a pentahydroxy flavone from Ponderosa Pine Bark and concluded that it should have the constitution of 3:5:8:3′:4′-pentahydroxy flavone. The properties recorded in this paper for the synthetic pentahydroxy flavone, its acetate and methyl ether do not agree with those of the natural product and its derivatives.

Experimental

5:8-*Dimethoxy flavanone* (*I* a)

2-Hydroxy-3:6-dimethoxy chalkone[3] (1·5 g.) was refluxed with alcohol (100 c.c.) and conc. sulphuric acid (2·5 c.c.) for 35 hours, diluted with water (100 c.c.) and the alcohol distilled off under reduced pressure. The solid product crystallised from ethyl acetate as colourless prismatic needles and rods, m.p. 163–64° C. Yield, 1·0 g. (Found: C, 71·7; H, 5·6; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). It gave no colour with alcoholic ferric chloride solution.

3-*Hydroxy*-5:8-*dimethoxy flavone* (*II* a)

The dimethoxy flavanone (0·5 g.) was dissolved in alcohol (50 c.c.) and to the boiling solution iso-amyl nitrite (3 c.c.) and conc. hydrochloric acid (30 c.c.) were added alternately in small quantities at a time, with stirring. The solution turned bright yellow first and finally bright reddish orange. The hot solution was allowed to cool slowly and stand for 2 hours with occasional shaking. It was then diluted with water (200 c.c.) and within a few minutes crystals of the flavonol separated out. This was filtered off and crystallised from ethyl alcohol as yellow needles and long rectangular plates, m.p. 191–92° C. Yield, 70 mg. (Found: C, 66·8; H, 4·5; $C_{17}H_{14}O_5$, $\frac{1}{2}H_2O$ requires C, 66·5; H, 4·9%). A further quantity (30 mg.) was obtained from the mother liquor which was extracted with ether. The ether solution was extracted with sodium hydroxide (2%) and the alkaline solution acidified and re-extracted with ether. On distilling off the solvent an oil was obtained. It was heated with a mixture of glacial acetic acid and concentrated hydrochloric acid (1:1; 10 c.c.) on a water-bath for 30 minutes. On dilution with water a solid product was obtained which on crystallisation from ethyl

alcohol melted at 191–92°. It gave a brown colour with alcoholic ferric chloride solution.

3 : 5 : 8-*Trimethoxy flavone* (*III* a)

3-Hydroxy-5 : 8-dimethoxy flavone (0·8 g.) was dissolved in acetone (150 c.c.) dimethyl sulphate (0·4 c.c., excess) and ignited potassium carbonate (2 g.) added and the mixture refluxed for 8 hours. The solution was filtered off, the solvent evaporated and the residue treated with water to decompose the excess of dimethyl sulphate. The solid product gave no colour with alcoholic ferric chloride solution and crystallised from methyl alcohol as pale yellow stout prisms melting at 169–70° alone or admixed with the sample prepared earlier.[1] Yield, 0·8 g. In the earlier description of the trimethoxy flavone the melting point was wrongly reported as 121–22°. On re-examination of the sample it was found to melt at 169–70°. The lower melting point seems to be therefore an error.

2-*Hydroxy*-ω : 3 : 6-*trimethoxy acetophenone* (*IV*)

The above flavone (0·6 g.) was dissolved in absolute alcoholic potash (50 c.c.; 8%) and the solution refluxed over a water-bath for 8 hours. The alcohol was then distilled off and the residue treated with water (50 c.c.). The alkaline solution was extracted with ether to remove any unchanged product, acidified with hydrochloric acid and re-extracted with ether. The ether solution was washed with sodium bicarbonate and then with water. After the ether was distilled off, the residue crystallised from dry ether as deep yellow elongated and stout rectangular prisms, m.p. 102–3° C. Yield, 0·2 g. It gave a green colour with alcoholic ferric chloride solution (Found: C, 57·9; H, 5·9; $C_{11}H_{14}O_5$ requires C, 58·3; H, 6·2%).

3 : 5 : 8 : 3′ : 4′-*Pentamethoxy flavone* (*Allan-Robinson condensation*) (*III* b)

An intimate mixture of the above ω-methoxy ketone (1 mol; 0·15 g.), veratric anhydride (2·5 mol; 0·58 g.), sodium veratrate (1·6 mol; 0·25 g.) was heated under reduced pressure at 170–80° for two and a half hours. The cooled product was dissolved in alcohol (36 c.c.) and water (3 c.c.) containing sodium hydroxide (3·7 g.), and the solution refluxed for 15 minutes. The alcohol was then removed under reduced pressure, and water (35 c.c.) added, when the pentamethoxy flavone separated out. It crystallised from ethyl alcohol as very pale yellow needles and rectangular prisms, and melted at 154–55° C.

5 : 8 : 3′ : 4′-*Tetramethoxy flavanone* (*I* b)

2-Hydroxy-3 : 6 : 3′ : 4′-tetramethoxy chalkone (1 g.) was dissolved in alcohol (100 c.c.) and concentrated sulphuric acid (2·5 c.c.) added. The

mixture was refluxed for 40 hours, and the product worked up as in the earlier case. The flavanone crystallised from a mixture of ethyl acetate and petroleum ether as colourless prismatic needles and rods; m.p. 141–42° (Found: C, 66·2; H, 5·6; $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·8%).

3-Hydroxy-5 : 8 : 3′ : 4′-tetramethoxy flavone (*II* b)

The tetramethoxy flavanone (0·5 g.), alcohol (40 c.c.), iso-amyl nitrite (3 c.c.) and concentrated hydrochloric acid (30 c.c.) were used according to the procedure already described. The main yield of the flavonol crystallised from methyl alcohol as yellow rectangular plates; m.p. 184–85°. Yield, 50 mg. (Found: C, 63·3; H, 5·2; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%). A further quantity (50 mg.) was obtained by working up the mother liquor as already described. The flavonol gave a brown colour with alcoholic ferric chloride.

The acetate was prepared by heating the above product with acetic anhydride and a drop of pyridine. It crystallised from ethyl acetate-petroleum ether mixture as almost colourless thick rhombohedral plates, m.p. 178–79°.

3 : 5 : 8 : 3′ : 4′-Pentamethoxy flavone (*III* b)

The methylation of the above flavonol (50 mg.) was carried out using acetone (50 c.c.), dimethyl sulphate (0·43 c.c., excess) and potassium carbonate (1 g.) according to the procedure already given. The pentamethyl ether crystallised from a mixture of ethyl acetate and petroleum ether as very pale yellow needles and rectangular prisms; m.p. 154–55° C. Mixed melting point with the sample prepared by the Allan-Robinson method was undepressed. Yield, 40 mg. (Found: C, 64·4; H, 5·3; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%).

3 : 5 : 8 : 3′ : 4′-Pentahydroxy flavone

5 : 8 : 3′ : 4′-Tetramethoxy-3-hydroxy flavone (0·2 g.) was dissolved in acetic anhydride (5 c.c.) and to the cooled solution was added hydriodic acid (5 c.c.) carefully. The solution was refluxed for two hours in an oil-bath at 145–50°. It was then poured into crushed ice and treated with a saturated solution of sodium bisulphite (15 c.c.). The solid product was filtered and crystallised from dilute methyl alcohol when it separated as yellow tiny prisms; m.p. 265–66° with sintering at 248–50° C. Yield, 0·1 g. (Found: C, 59·3; H, 2·9; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%). With alcoholic ferric chloride it gave an olive green colour changing to olive brown; solutions in aqueous sodium hydroxide and carbonate had an orange colour which faded.

The *acetate* was prepared by heating the above product with acetic anhydride and a drop of dry pryridine. It crystallised from a mixture of methyl alcohol and ethyl acetate as lens-shaped crystals; m.p. 233–35° C.

The pentahydroxy flavone was remethylated in acetone solution with excess of dimethyl sulphate and potassium carbonate. The methyl ether crystallised from a mixture of ethyl acetate and petroleum ether, m.p. 154–55° C. Mixed melting point with pentamethoxy flavone obtained by the methylation of 5 : 8 : 3′ : 4′-tetramethoxy flavonol and by the Allan-Robinson method was undepressed.

Our thanks are due to Dr. S. K. Mukerjee for microanalysis.

SUMMARY

Starting from 2-hydroxy-3 : 6-dimethoxy acetophenone a new synthesis of 3-hydroxy primetin has been effected and by alkali fission of the trimethyl ether 2-hydroxy-ω : 3 : 6-trimethoxy acetophenone has been prepared. Using the same procedure (modified Kostanecki's method) 3 : 5 : 8 : 3′ : 4′-pentahydroxy flavone, its pentamethyl ether and penta-acetate have been obtained. The properties of these compounds are different from those of the pentahydroxy flavone and its derivatives obtained from Ponderosa Pine Bark.

REFERENCES

1. Seshadri, Varadarajan and Venkateswarlu .. *Proc. Ind. Acad. Sci.*, 1950, **32A**, 250.
2. Kohli, Mukerjee and Seshadri .. *J.S.I.R.* (Under publication).
3. Ballio and Pocchiari .. *Br. Chem. Abs.*, 1951, **A II**, 763; *Ric. Sci.*, 1950, **21**, 1301.
4. Row and Seshadri .. *Proc. Ind. Acad. Sci.*, 1945, **21A**, 132.
5. Kurth and Hubbard .. *Ind. Eng. Chem.*, 1951, **43**, 896.

ANALYSIS AND CHARACTERISATION OF THE OIL FROM THE SEEDS OF *THESPESIA POPULNEA*

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Thespesia populnea is commonly known as the 'Indian Tulip'. It is a species belonging to the botanical family of *Malvaceæ*, and is an evergreen tree of moderate size. It has a dry fruit which contains a number of seeds. It grows in the coast forests of India, by roadside, especially in Madras.

A. K. Menon[1] extracted a dark red oil from seeds and reported a 19·6% yield of oil calculated on the whole seed. The same author determined also some of the characteristics of the oil. Apart from a preliminary investigation, the author has not reported any further work. The oil is used in India in the treatment of cutaneous infections. Neelakantan, Rao and Seshadri[2] worked on the chemical components of the flowers of *Thespesia populnea* and isolated three yellow pigments Populnin, Populnetin and Herbacetin along with a colourless phenolic compound Populneol.

The purpose of this investigation was to determine the characteristics of the oil from the seeds and to make a quantitative estimation of its component fatty acids.

Characteristics of the Oil

Seeds used in this work were obtained from the Chepauk area in Madras and were fully ripe. The oil was obtained from the seeds by extracting the finely ground meal with light petrol (b.p. 45–65°) and removing the solvent under reduced pressure. The oil had a dark red colour, a syrupy consistency and a faint agreeable odour. The seeds contained about 20% oil.

The physical and chemical constants of the oil were:

TABLE I

Specific Gravity (28°)	0·9251
Iodine value (Hanus)	71·5
Saponification value	203·2
Acetyl value	inappreciable
Acid value	0·53
Unsaponifiable matter % ..	0·72
Reichert-Meissel value ..	5·5
Reichert-Polenske value ..	0·37
Oil content of seed %	20·0

DETERMINATION OF FATTY ACIDS

This was carried out by the ester fractionation method. The oil was saponified with KOH and the mixed acids, after the removal of unsaponifiable matter, were separated into saturated and unsaturated fractions by the lead salt method. The free acids from the saturated fraction had an iodine value of 4·5, and they represented 22·2% of the total acids. The free fatty acids from each fraction were converted into the methyl esters and the methyl esters were fractioned. The data are reported in Tables II, III and IV.

TABLE II

Fractional Analysis of Methyl Esters of the Solid Acids

Solid acids 22·2% of total mixed acids

Fraction	Weight gm.	Boiling point ° C. at about 5 mm. Hg	S.E.	I.V.	Saturated acids			Oleate
					C_{14}	C_{16}	C_{18}	
S_1 ..	1·61	150–164	260·1	0·81	0·73	0·86		0·02
S_2 ..	4·2	164–166	271·5	2·5		3·8	0·28	0·12
S_3 ..	5·5	166–168	271·9	3·4		5·15	0·13	0·22
S_4 ..	1·42	168–170	272·7	4·2		1·34	0·01	0·07
S_5 ..	2·7	170–176	276·2	6·8		2·15	0·34	0·21
Residue ..	1·5		284·5	8·1		0·68	0·68	0·14
Wt. ester ..	16·93				0·73	13·98	1·44	0·78
Wt. acids ..	16·05				0·69	13·25	1·37	0·74
% acid in fraction ..	100·0				4·3	82·6	8·5	4·6
% acid in total mixed acids	22·2				1·0	18·3	1·9	1·0

TABLE III

Fractional Analysis of Methyl Esters of the Liquid Acids

Liquid acids 77·8% of total mixed acids

Fraction	Weight gm.	Boiling point ° C. at about 5 mm. Hg	S.E.	I.V.	Satd. acids	Unsatd. acids	
					C_{16}	C_{18}^{u}	C_{18}^{2u}
L_1 ..	5·12	160–180	281·3	60·9	2·62	1·4	1·1
L_2 ..	20·43	180–182	293·6	135·2		8·81	11·62
L_3 ..	10·86	182–185	294·2	135·9		4·59	6·27
L_4 ..	19·35	185–190	294·8	136·4		8·07	11·28
L_5 ..	6·78	190–200	295·5	139·1		2·62	4·16
Residue ..	3·56		295·5	142·2		1·25	2·31
Wt. esters ..	66·1				2·62	26·74	36·74
Wt. acids ..	62·96				2·48	25·48	35·0
% acid in fraction ..	100·0				3·9	40·5	55·6
% acid in total mixed acids ..	77·8				3·1	31·5	43·2

TABLE IV

Fractional Analysis Summary

Acid	Solid Fraction	Liquid Fraction	Total
Myristic	1·0	..	1·0
Palmitic	18·3	3·1	21·4
Stearic	1·9	..	1·9
Oleic	1·0	31·5	32·5
Linoleic	..	43·2	43·2

In computing unsaturated or liquid fractions (denoted by L in the Tables) the following assumptions were made:—

1. For fractions containing methyl oleate, methyl linoleate and esters of saturated acids the assumption was made that the oleate and linoleate distil in the same ratio as in the first pure C_{18} unsaturated esters.

2. For fractions consisting only of pure C_{18} unsaturated esters the calculations were based on the iodine values alone.

SUMMARY

The seeds of *Thespesia populnea* yield a semi-drying oil which has a dark red colour and a faint agreeable odour. The mixed fatty acids consist of myristic, palmitic, stearic, oleic and linoleic acids, the last two being the major constituents.

The fact that *Thespesia populnea* seeds contain about 20% oil, focuses attention on the potentialities of the seeds as a source of oil of industrial importance.

ACKNOWLEDGMENT

The author takes this opportunity to express his deep gratitude to Prof. K. N. Menon for guidance during the course of this investigation.

LITERATURE CITED

1. Menon, A. K. .. *J. Soc. Chem. Ind.*, 1910, **29**, 1431.
2. Neelakantan, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1943, **17A**, 26

THE STEP-WISE ADSORPTION OF NITROGEN ON CARBON BLACK[a]

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Abstract

Adsorption measurements have been carried out for nitrogen on the commercial carbon blacks Spheron 6 and Vulcan. The adsorption on Spheron 6 is step-wise in the pressure range 0 to 45 mm. (fraction of surface covered approximately 10^{-5}), and on Vulcan to at least 0·16 mm.

Calorimetric measurements of differential heats of adsorption on Spheron 6 have shown that they vary with the amount of surface covered being greatest at low coverages and decreasing toward the heats of liquefaction as a limit.[1,2] This indicates that the surface of such materials contains various types of adsorption sites, having different heats of adsorption, and suggests that sufficiently refined measurements would show a step-wise adsorption isotherm. This paper reports the results of experimental studies of the adsorption of nitrogen on the carbon blacks Spheron 6 and Vulcan in the pressure range 0·00 to 75 mm., and at 0° and 100° C.

Experimental

In the earliest series of measurements, carried out by the first author, the apparatus was of conventional design. It consisted of a sample container attached to a gas burette, nitrogen reservoir, manometer, and a small MacLeod gauge. The gas burette was cylindrical in shape and had a volume of about 370 c.c. The heights of the various mercury columns were read to the nearest 0·1 mm. with a cathetometer.

The nitrogen was obtained from air by shaking a container partially filled with alkaline pyrogallol solution in order to remove the oxygen and

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[a] This paper contains some of the material presented in the M.A. thesis of J. Garelick (Buffalo, February 1948) and in the Ph.D. thesis of H. B. Kirkpatrick (Buffalo, June 1951). It was presented at the December 1953 meeting of the Indian Academy of Sciences in Ahmedabad.

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carbon dioxide. Water vapour was removed by freezing it out in a liquid nitrogen trap placed between the reservoir bulb and the gas burette.

The carbon black sample was a standard commercial grade manufactured by the Godfrey L. Cabot Co., and designated Spheron Grade 6. The sample was out-gassed by heating it at a temperature of 400° C. for 20 hours, followed by 1 hour at 650°.

In a later series of measurements by the third author, similar, but more refined, apparatus was employed. The whole assembly of gas reservoir, burette, and MacLeod gauge was enclosed in a constant temperature air-bath maintained at 32° ±0·8° C. The side-arm of the MacLeod gauge was permanently evacuated to eliminate compression effects, and it had three parallel branches made from 11, 7 and 5 mm. glass tubing. The compression tube on the body of the gauge was divided into three segments, of different diameters, matching those of the side arms. A second side-arm

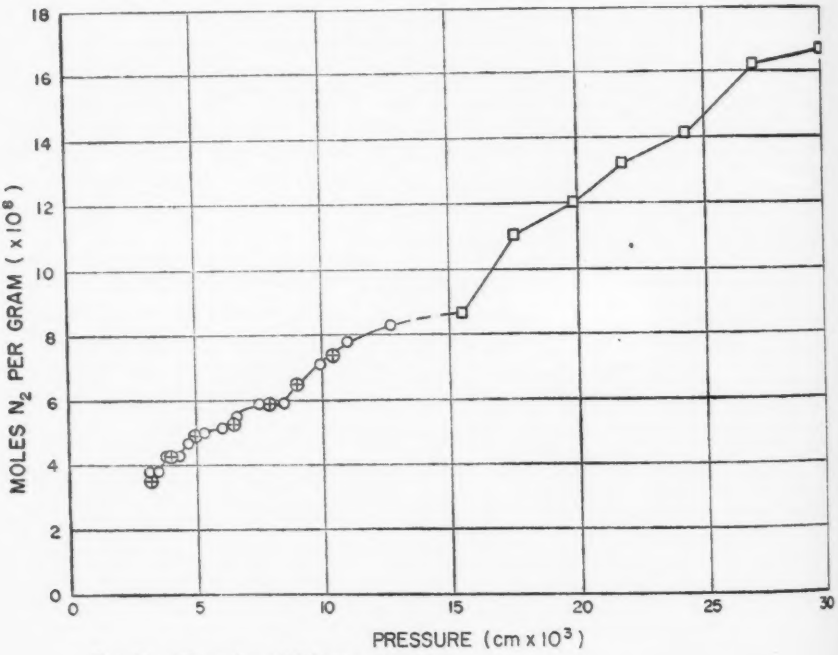

FIG. 1. Adsorption of Spheron 6 at 0° C.

First Run Adsorption O
Desorption ⊕

Second Run □

connected the body of the gauge to the rest of the system. With this gauge it was possible to measure pressures ranging from 10^{-5} mm. to about 30 mm. The sample temperature was controlled by an ice-bath or liquids boiling under reflux.

The adsorbate gas was tank nitrogen purchased from the Linde Air Products Co. In order to remove whatever oxygen might be present, the

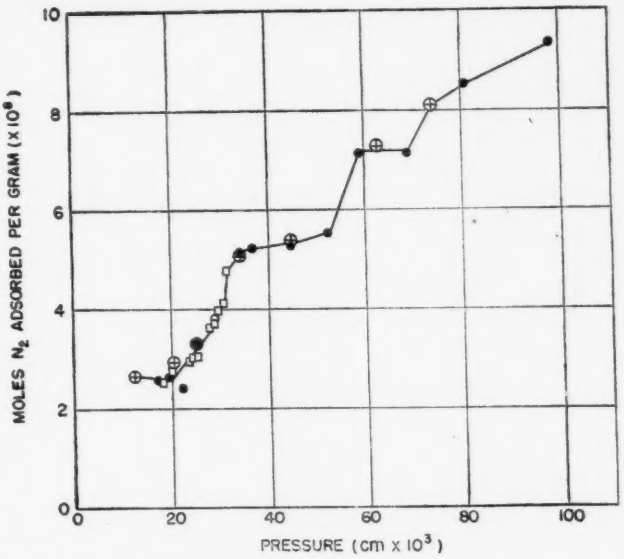

FIG. 2. Adsorption on Spheron 6 at 100° C.

First Run — Adsorption ●
Desorption ⊕

Second Run (Adsorption) □

nitrogen was passed over hot copper gauze which had been previously reduced with hydrogen. No attempt was made to remove inert gases because they have a negligible tendency to become adsorbed at the low pressures used in these experiments.

All the carbon black samples were out-gassed at a temperature of 475° C. This relatively low temperature was chosen in order to avoid the changes in structure and adsorption behaviour which carbon black is reported to undergo when heated at 700° and higher.[3, 4, 5] At this temperature several months of pumping were required to evacuate the samples thoroughly enough for adsorption measurements in the low pressure range. Despite

this precaution changes in the surface behaviour of the carbon blacks were encountered and for this reason the isotherms were all measured at 0° and no attempt was made to calculate heats of adsorption. The first sample was evacuated to a pressure of 10^{-3} mm. and succeeding ones to about 10^{-4}.

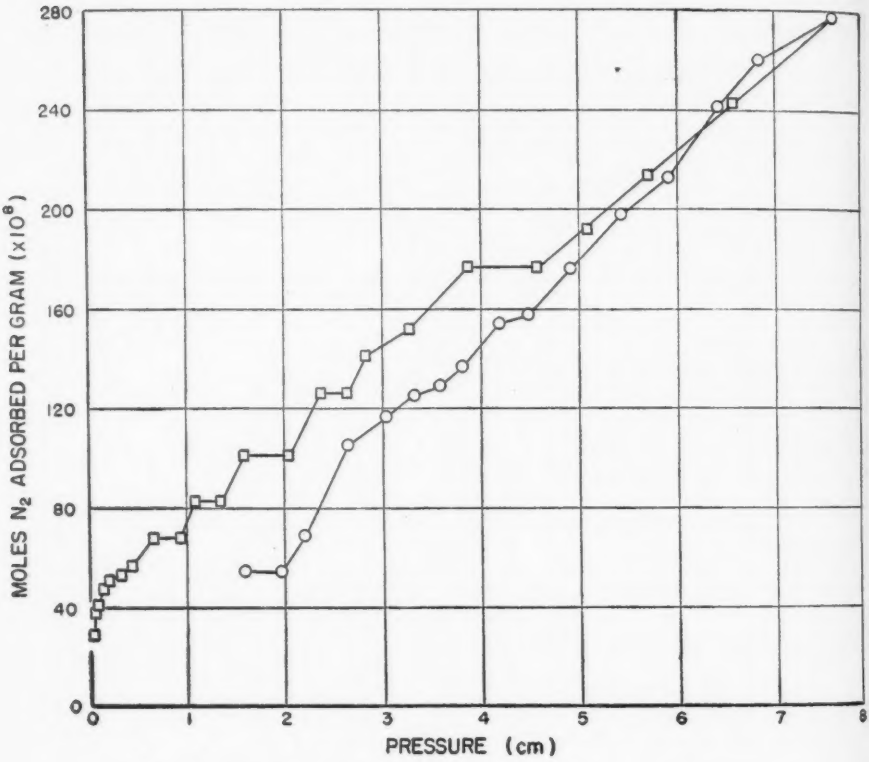

FIG. 3. Adsorption on Spheron 6 at 0°.
Adsorption O
Desorption □

RESULTS

I. Experiments by the First Author

The adsorption isotherms on Spheron Grade 6 in the pressure range 0–1 mm., at 0° C. and 100° C., are shown in Figs. 1 and 2. The step-wise nature of the adsorption is clearly evident. There is good agreement between the values obtained on adsorption and desorption, except at the very

lowest end of the isotherms (about 3×10^{-8} moles N_2 per gram), and no indication of hysteresis. In the 100° isotherm there is observed at about 0·53 mm. a prominent step whose contours are qualitatively similar to one observed at 0° and 0·58 to 0·67 mm. in the later experiments by the third author.

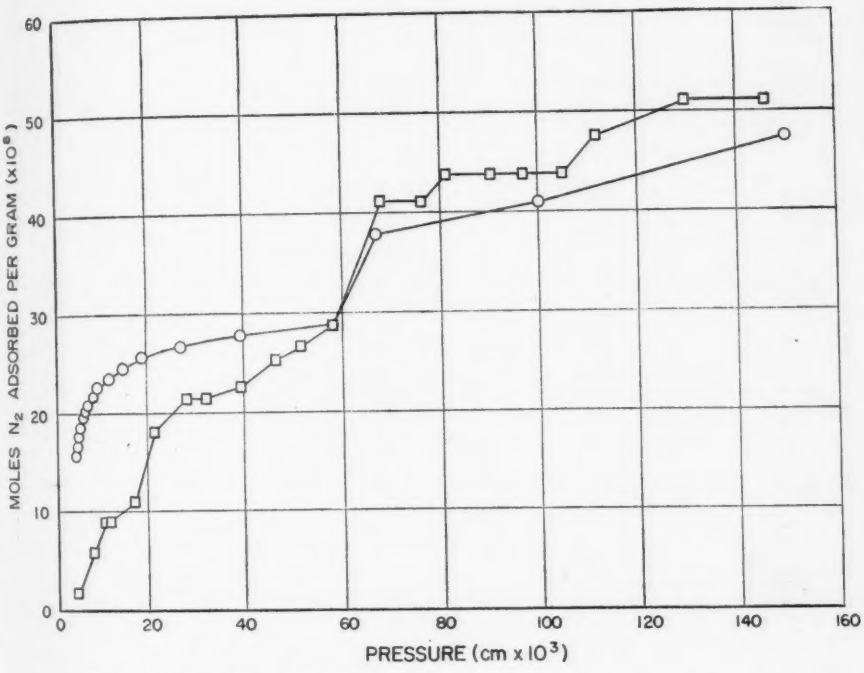

FIG. 4. Adsorption on Spheron 6 at 0°.
First Sample O
Second Sample □

II. Experiments by the Third Author

First Sample of Spheron 6.—The adsorption data at 0° C., in the pressure range 4×10^{-3} cm. to 8 cm., are shown in Figs. 3 and 4.

The adsorption was approximately linear at pressures greater than about 4·5 cm., and exhibited sharp irregularities or " steps " in the range 4·5 cm. to 0·058 cm. At 0·58 mm. there was a very prominent step and below this pressure the isotherm was a smooth curve. The points for desorption show hystersis.

Second Sample of Spheron 6.—The isotherm for this sample is also shown in Fig. 4. The large step at 0·58 mm. was again observed; but below this pressure the adsorption continued step-wise instead of being a smooth curve as in the first sample.

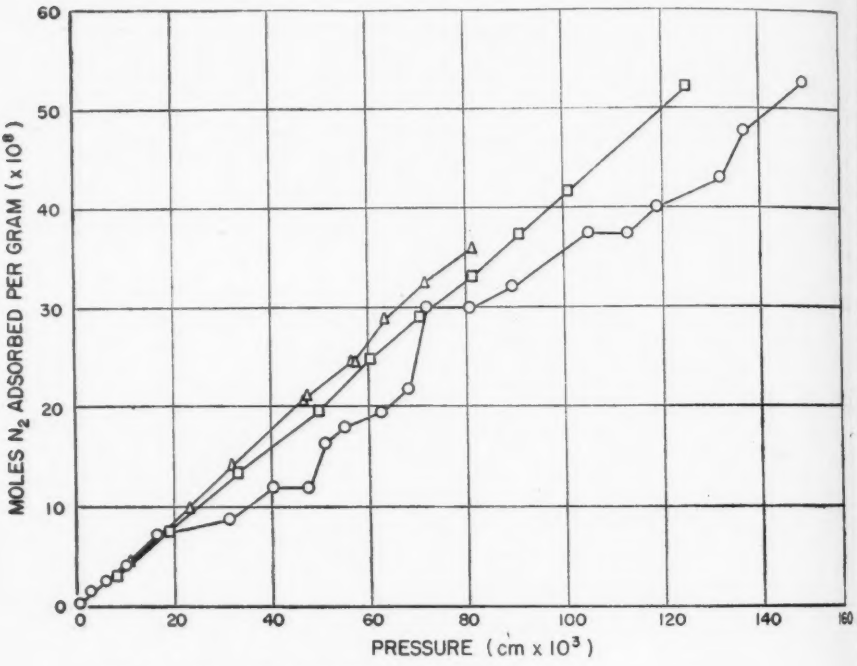

FIG. 5. Adsorption on Third Sample of Spheron 6.
First Run O
Second Run □
Third Run △

Third Sample of Spheron 6.—Fig. 5 shows the results of three successive runs on this sample. This sample and the second one were out-gassed simultaneously, both being removed from the out-gassing apparatus by sealing off under vacuum. The third sample then stood under vacuum for about 1 week while measurements were being made on the second. The isotherm obtained in the first run has certain features similar to that of the second sample, but the overall adsorption is less and the pressure for a definite amount of adsorption is higher. In this case the large step occurred at 0·68 mm. instead of at 0·58 mm. as in the first two samples.

After the first run the sample was evacuated at 250° for 24 hours. This treatment produced a startling change in the adsorption. The overall adsorption increased slightly and the isotherm became essentially linear in form, with only a slight trace remaining of the large 0·6 mm. step.

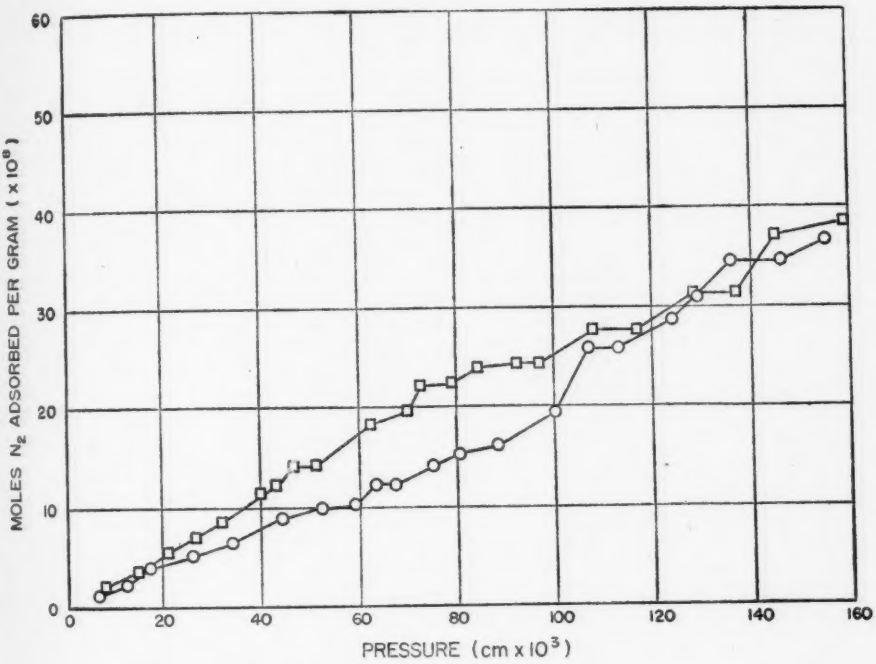

FIG. 6. Adsorption on Vulcan at 0°.
First Run O
Second Run □

The sample was then re-evacuated for 5 days at 475°. After this treatment the overall adsorption was again somewhat increased and the isotherm was linear up to about 0·47 mm. At 0·57 mm. there was a definite break and the large step seems to have been partially restored.

Vulcan Sample

The results for this sample are shown in Fig. 6. The adsorption was again observed to be step-wise, although less markedly so than in the case of Spheron 6. There was a small step at 0·59 mm. which may correspond to the large step observed at about 0·6 mm. in the Spheron samples.

A second run was carried out after evacuating the sample for 7 days at 475°. Once more the total adsorption increased somewhat and the profile of the isotherm changed, the steps becoming less pronounced.

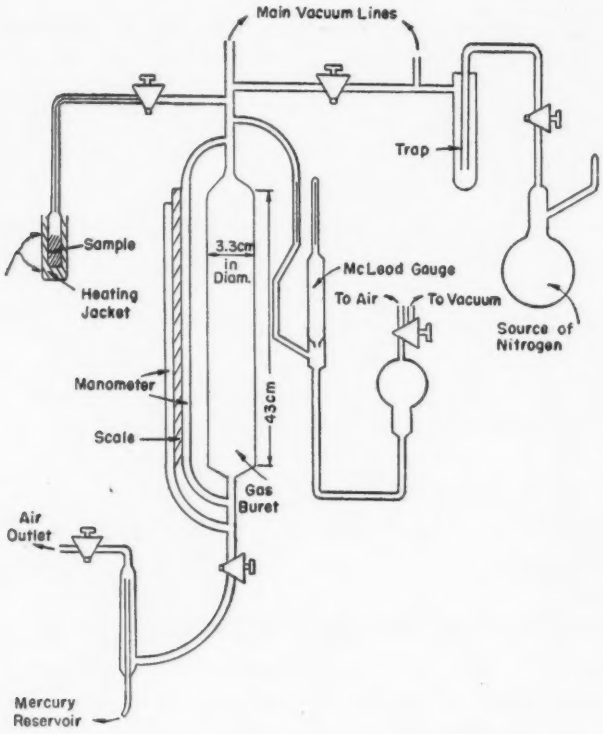

FIG. 7. Original Adsorption Equipment used by J. G.

DISCUSSION

Beebe and his co-workers have carried out calorimetric determinations of the differential heats of adsoprtion on Spheron 6 and have shown that they vary with the amount of surface covered. The heat of adsorption is greatest at low coverages; as the surface becomes filled in, it decreases, at first rapidly and then slowly, approaching the heat of liquefaction as a limit. These results, in conjunction with those of the present investigation, show that the surface is not uniform and that it seems to consist of regions having different adsorptive capacities and heats of adsorption. Those regions

having the highest heat of adsorption are the ones on which initial adsorption takes place. After these sites are covered, those having the next highest heat of adsorption begin to fill in, and the process continues in this manner until the monolayer is complete, or at least until the adsorption is occurring on a uniform general surface. The breaks observed in the isotherms correspond to the saturation of one class of adsorption sites and the

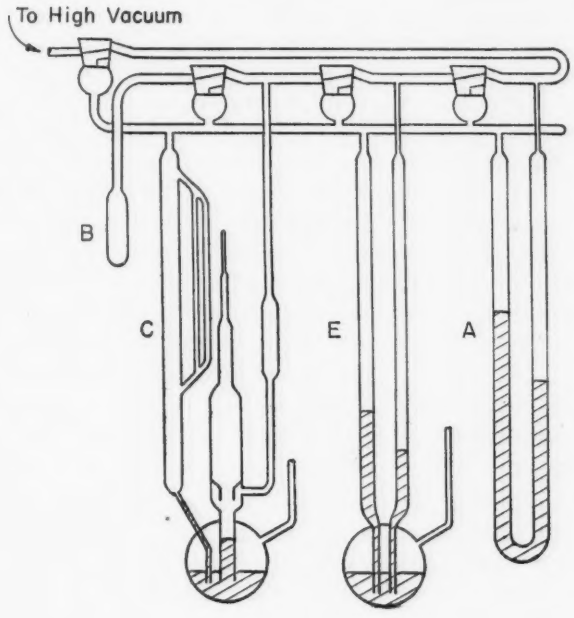

FIG. 8. Adsorption Equipment used by H.B.K.

A Nitrogen Reservoir
B Sample Container
C MacLeod Gauge
D Gas burette

beginning of adsorption of a new one. The different classes of sites probably consist of crystallite faces, crevices and the edges of graphitic layers.

It has been pointed out in the statement of results that increasing the time of de-gassing increases to overall adsorption, and that allowing the sample to stand for about one week under vacuum at room temperature

has the effect of increasing the pressure for a given amount of adsorption.

The best explanation for these observations seems to lie in the ideas advanced by S. Chu Liang in an investigation of the adsorption of inert gases by glass.[6] Following Liang, if one considers a heterogeneous surface previous to evacuation, it may be thought of as being composed initially of adsorption sites having some distribution of adsorptive activity and covered with chemisorbed gases. As evacuation at a high temperature proceeds, sites of higher and higher activity are uncovered and made available for physical adsorption. Thus with longer, or repeated, evacuations at high temperatures the quantity of gas adsorbed may be expected to increase as observed here in the third Spheron 6 sample and the Vulcan sample. The high temperature evacuation produces a surface in which the low activity adsorption sites are for the most part uncovered and most of the high activity sites are still occupied, the remaining adsorbed gas being distributed in some statistical manner over the sites of different activities. It may happen, then, that the evacuation is continued at room temperature. Under this condition Liang suggests that " the activity distribution need not remain constant " and that the surface structure may change in such a manner as to bring about a decrease in the number of high activity sites and an increase in the number of low activity ones. This increase in the number of low activity sites results in a higher pressure's being necessary to bring about a given amount of gas adsorption.

If such surface changes as Liang describes were to occur in the case of carbon black on standing under partial vacuum at room temperature, they might well explain the difference in isotherms obtained with samples two and three. However it is difficult to imagine that a substance having the structure attributed to carbon black by Biscoe and Warren[3] would change its surface structure at any appreciable rate at room temperatures. Moreover the repeated observations of the large step at about 0·6 mm. indicate that the surface is relatively stable even at 475°.

However a partially evacuated substance standing under vacuum might reduce its surface free energy by the redistribution of adsorbed gas toward high energy adsorption sites as well as by structural changes and this seems a more likely explanation in the present case.

The striking difference in the isotherms of the first and second samples at pressures less than 0·58 mm. is perhaps due to the shorter out-gassing of the first sample, which produced a relatively more homogeneous surface.

ACKNOWLEDGMENT

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REFERENCES

1. R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell — *J. Am. Chem. Soc.*, 1947, **69**, 95 and 2294.
2. ———, G. L. Kington, M. H. Polley and W. R. Smith — *Ibid.*, 1950, **72**, 40.
3. J. Biscoe and B. Warren .. *J. Applied Phys.*, 1942, **13**, 364.
4. P. H. Emmett and R. B. Anderson .. *J. Am. Chem. Soc.*, 1945, **67**, 1492.
5. C. S. Dewey and P. K. Lefforge .. *Ind. Eng. Chem.*, 1932, **24**, 1045.
6. S. Chu Liang . *J. Phys. Chem.*, 1953, **57**, 84.

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